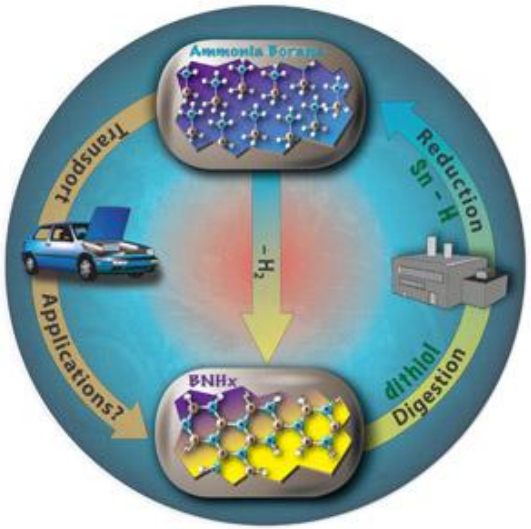
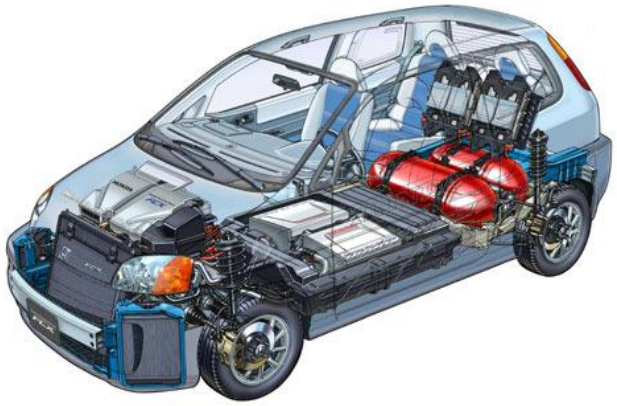
Pulling the Weight: Base Metal-Catalyzed Dehydrogenation of Amine-Borane Fuel Blends

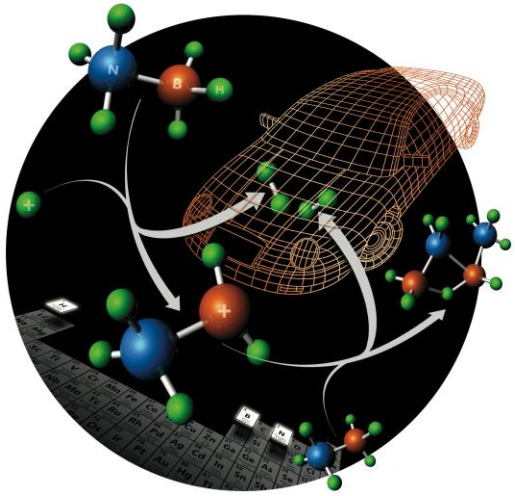
R. Tom Baker

University of Ottawa Chemistry Department and
Centre for Catalysis Research and Innovation

UMass IGERT lecture April 1, 2010







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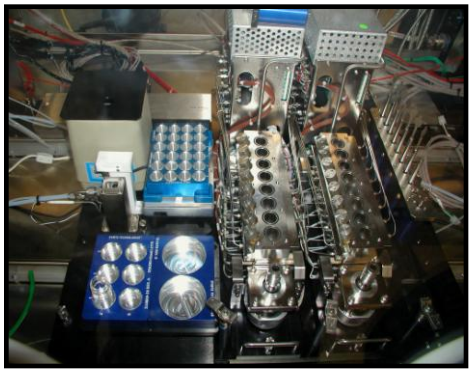
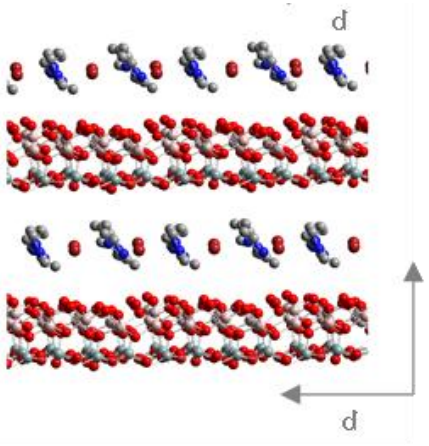
- The CCRI is a capability-based research center on two floors of Biosciences building with 27 faculty participants from Science, Engineering and Medicine
- Managed facilities include high throughput experimentation, materials characterization, and computational chemistry
- Research clusters include pharma/fine chemicals, energy applications, nanostructured catalysts, and biocatalysis
- Please visit us at http://www.catalysis.uottawa.ca/index-e.php





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Research Projects in the Baker Group

Hydrogen Production and Storage

- Catalyzed amine-borane dehydrogenation
- Electrocatalytic hydrogen production

Surface-Supported Molecules for Tandem Catalysis

- Allyl-Ir precursors for catalytic alkane dehydrogenation/H-X addition
- Allyl-Os precursors for alkene metathesis

'Soft' Biomass Conversion Catalysis

- Oxovanadium catalysts for selective C-C bond cleavage of lignin
- Iron catalysts for polyalcohol deoxygenation

'Green' Routes to Fluorocarbons

- Catalyzed hydrodimerization of *in situ*-generated hydrofluoroalkenes
- Early metal hydrofluorocarbenes as initiators for hydrofluoroalkene metathesis and polymerization

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Hydrogen as Energy Carrier for Transportation Applications

- Combination of hydrogen and air in a fuel cell produces water and electricity, with no NO_x, SO_x, CO_2 or particulates

- Apart from current expense, durability issues, and precious metal burden of fuel cells, problems facing hydrogen economy include:

How to produce it?

How to store it?

Hydrogen Storage

Gas and Liquid Storage Tanks

- *Advantages*: Today's state-of-the-art
- *Challenge*: Safety and efficiency (boil-off), volumetric capacity

Metal Hydrides

- *Advantages*: Reversible and compact
- *Challenge*: Heat management and reversible examples have low (3-5 wt%) storage capacities

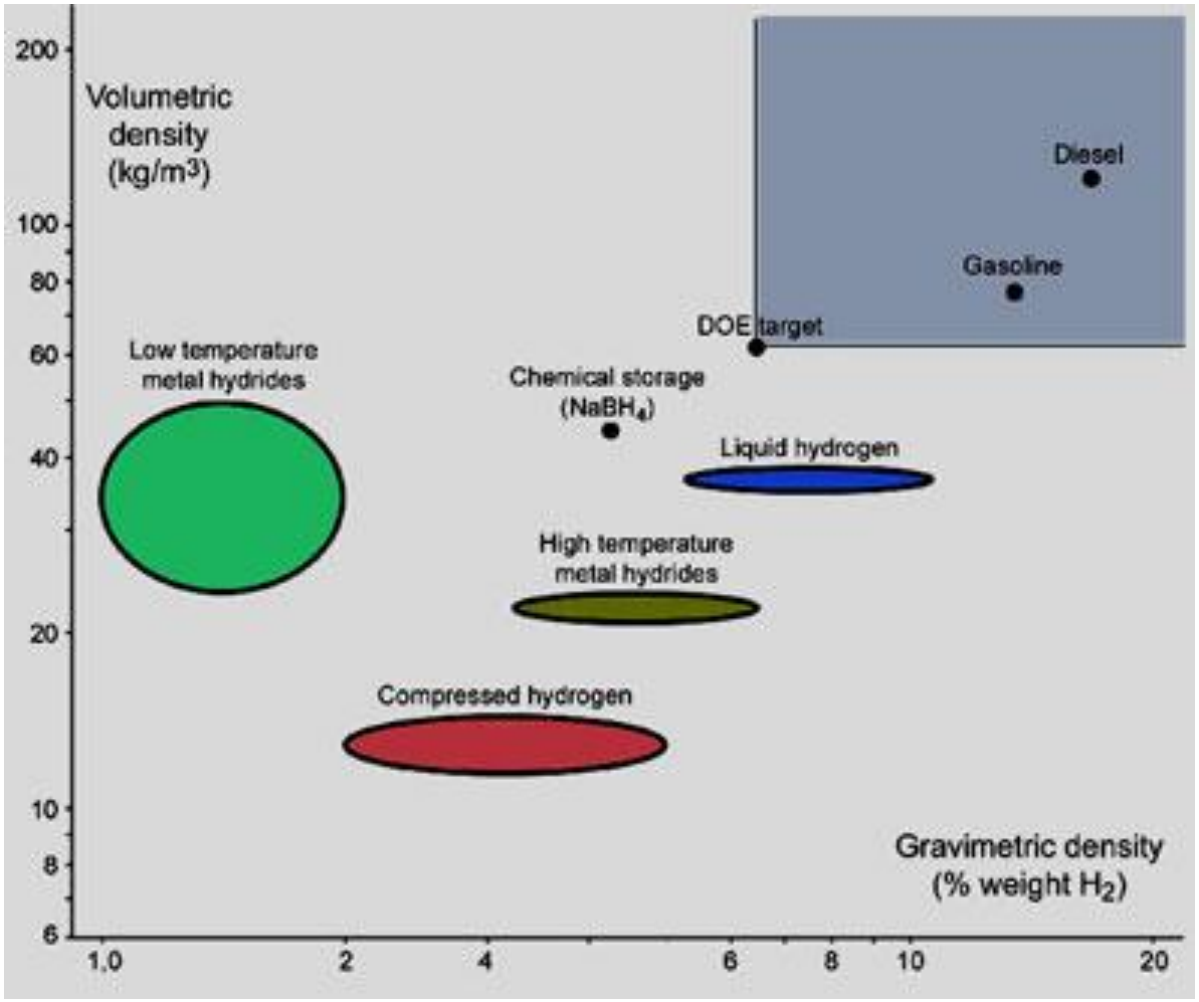
Physisorption

- *Advantages*: Fully reversible
- *Challenge*: Low storage capacity and low temperatures required

Chemical Hydrides

- *Advantages*: High storage capacities (generally > 8 wt%) that could meet DOE system goal of ≥ 6 wt%
- *Challenge*: Regeneration of spent fuel

Need Improved Fuel Density to use Hydrogen for Long-Haul Transportation



- In concert with energy and transportation industries, US Dept. of Energy set stringent targets (**5.5 wt.%H / 40 kg H_2 m^{-3}**) for H_2 storage to approach gas/diesel and funded three Centers of Excellence in 2005

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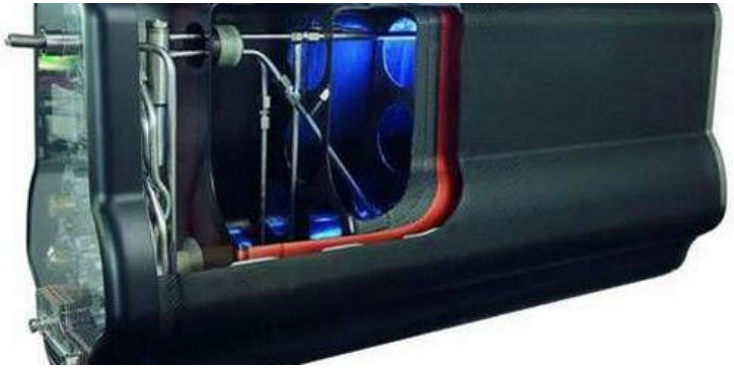
Improving Hydrogen Fuel Tanks

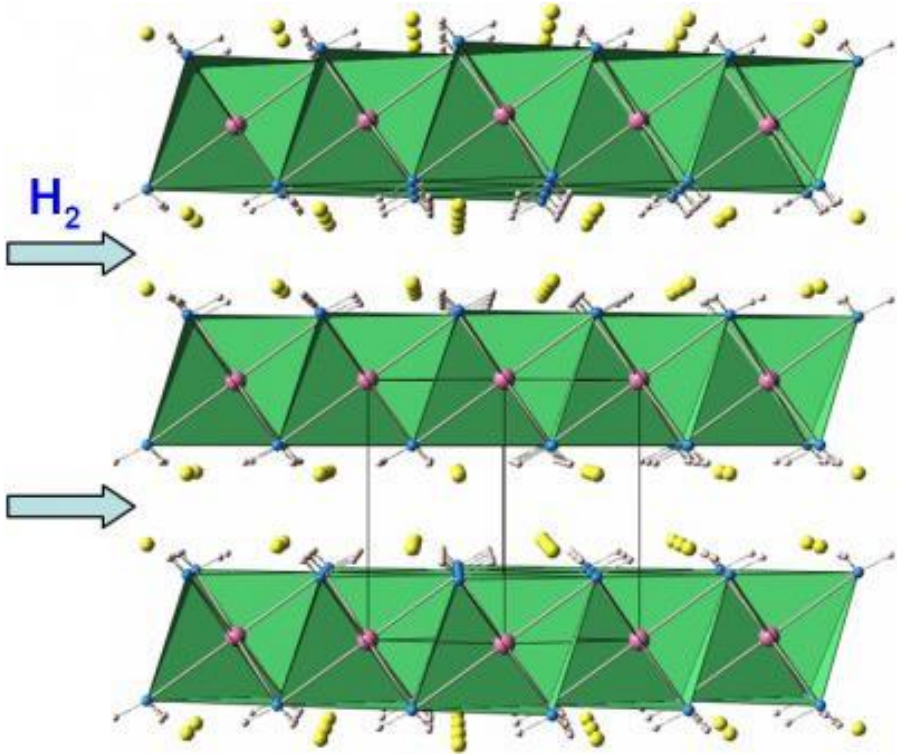
Carbon-fiber reinforced tank stores hydrogen at 10,000 psi at ambient temperatures

Lawrence Livermore National Lab's experimental car drove 650 miles on one fill of liquid hydrogen fuel (10 kg in 150 L tank stored at -400° F!)



BMW's new 'advanced composite' compressed H_2 tanks are integrated into vehicle side panels

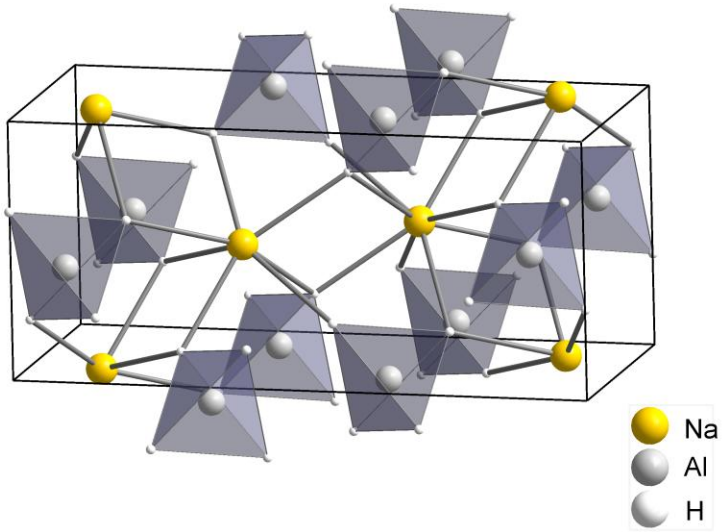
On-board Reversible Hydrogen Storage in Metal Hydrides

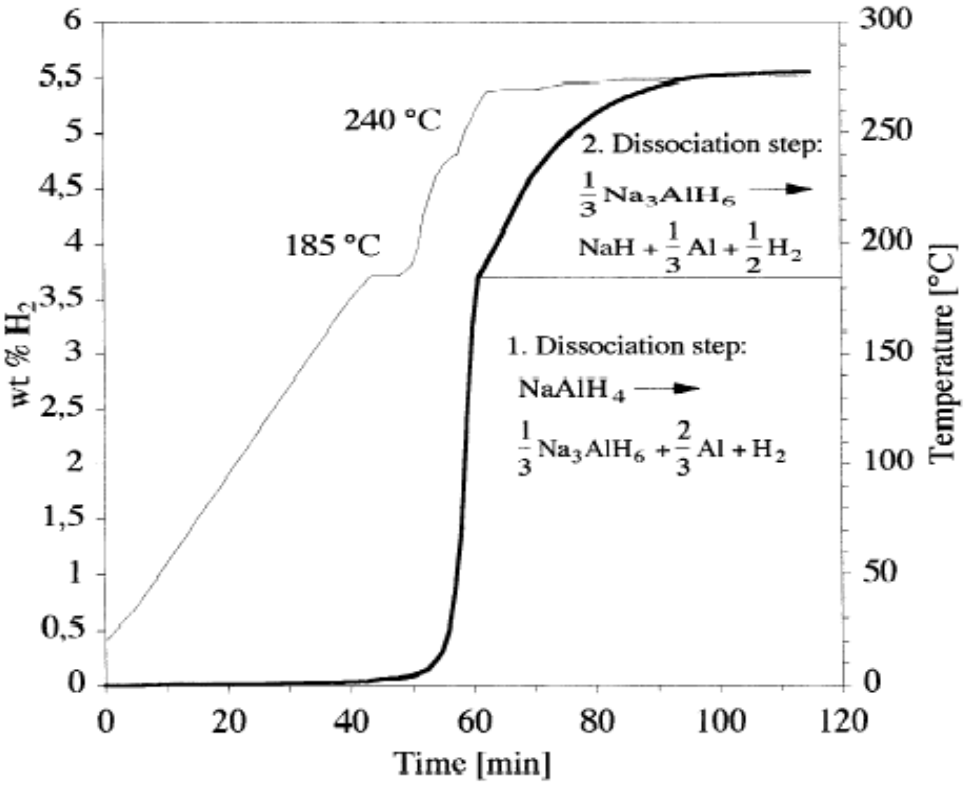


H. Wu. 'Structure of ternary imide $Li_2Ca(NH)_2$ and hydrogen storage mechanisms in amide-hydride system.' *J. Am. Chem. Soc*. **2008**, *130*, 6515.

Solid Sodium Alanate is Reversible Hydrogen Storage Material

Ti-doped sodium alanate is slowly reversible at 100 ^{0}C and 100 bar H_2)





- Thermodynamics cause significant T jump on refueling
- Associated tank cooling reduces storage capacity

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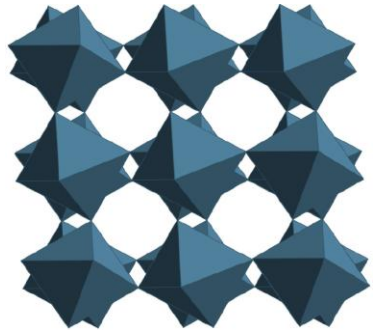
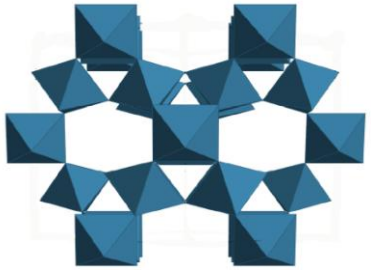
Alane, AlH_3, Offers Greater Storage Capacity

$$AlH_3 \rightarrow Al + 1.5H_2 \quad \text{10.1 wt.\%H; 120-150 °C}$$



α-AlH_3

$\rho = 1.48\ g/cm^3$



β-AlH_3

$\rho = 0.71\ g/cm^3$

γ-AlH_3

$\rho = 1.32\ g/cm^3$

Chemical synthesis under kinetic control:

$3LiAlH_4 + 4AlCl_3 \rightarrow 4AlH_3 + 3LiCl$

Carried out in ether solution

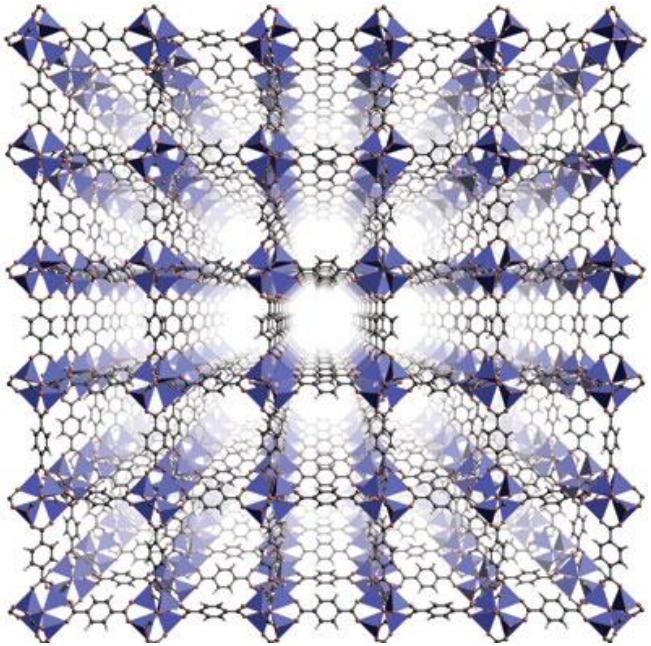
$Al_{(s)} + 1.5\ H_{2(g)} = AlH_{3(s)}$

$\Delta H \approx -10\ kJ\ mol^{-1}$

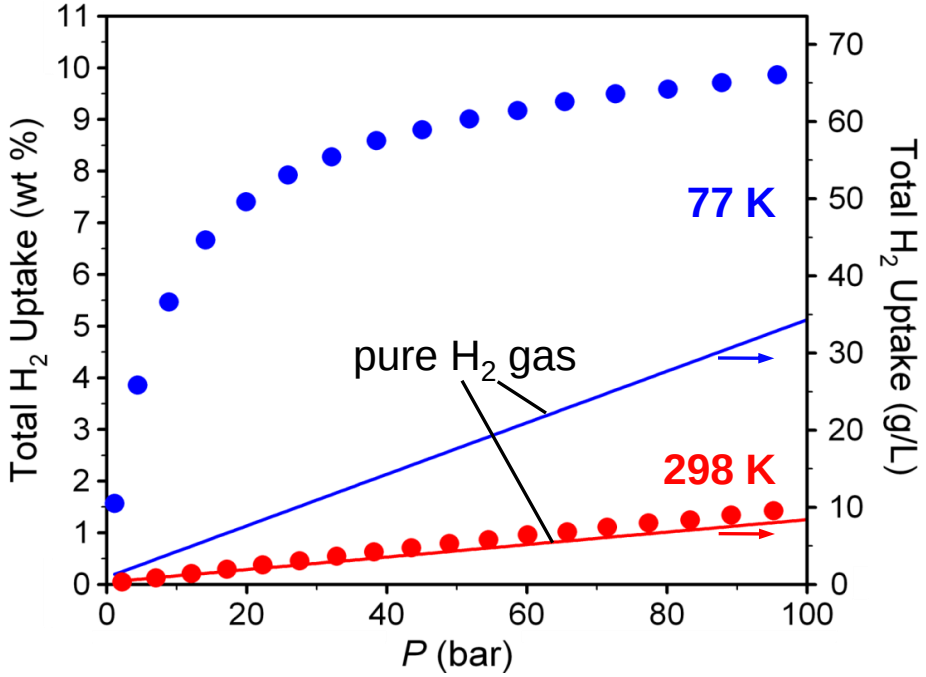
$\Delta S \approx -100\ J\ mol^{-1}\ K^{-1}$

- Currently need very high pressures to reform alane from Al

Cryogenic Hydrogen Storage in Metal-Organic Framework Materials

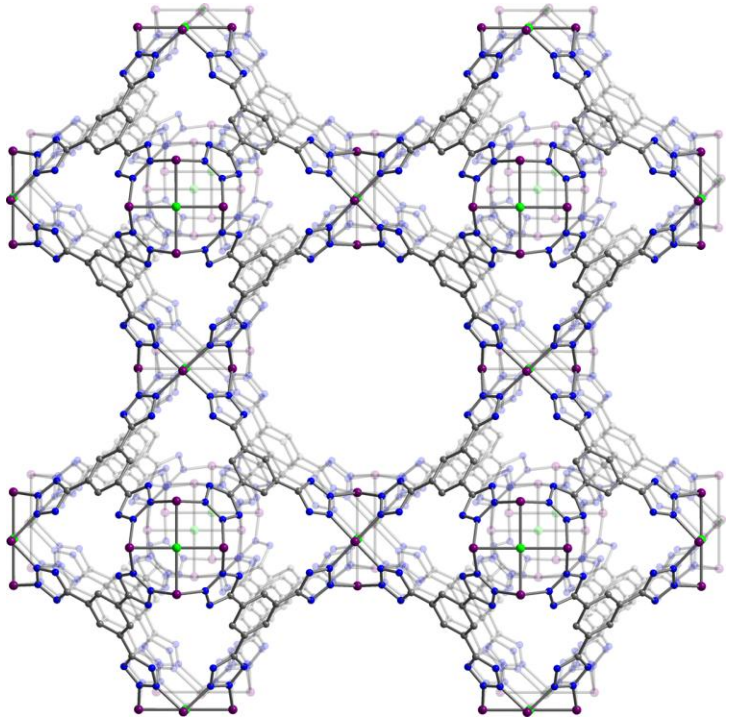


$Zn_4O(BDC)_3$ (MOF-5)

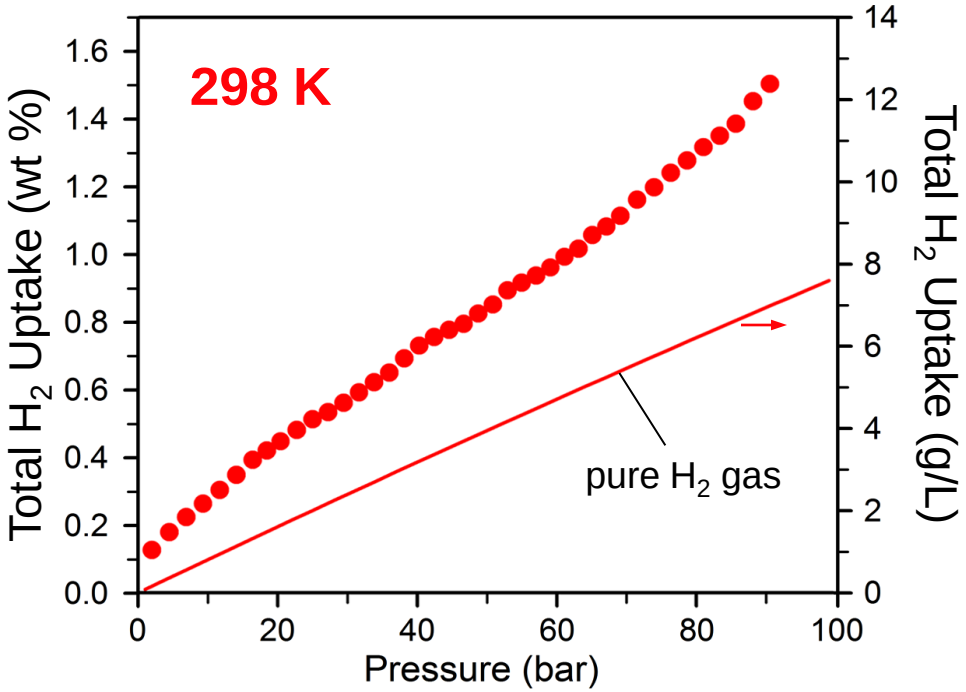


- Best overall properties yet achieved for cryogenic hydrogen storage
- Poor performance at 298 K owing to weak H_2 adsorption enthalpy (ca. -5 kJ/mol)

H_2 Storage in a MOF with Open Metal Sites



$Mn_3[(Mn_4Cl)_3(BTT)_8]_2$

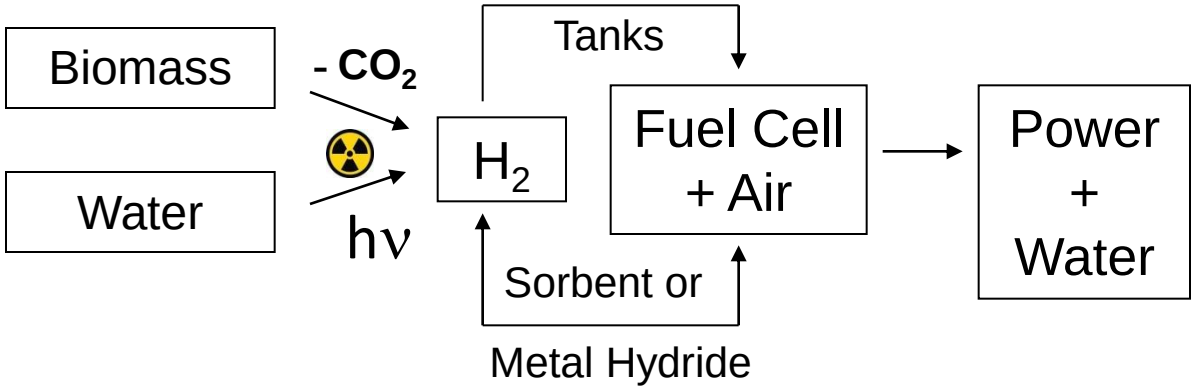


- Open Mn^{2+} sites on surface lead to stronger H_2 adsorption enthalpy (-12 kJ/mol)
- Highest volumetric storage density yet observed for a MOF at 298 K

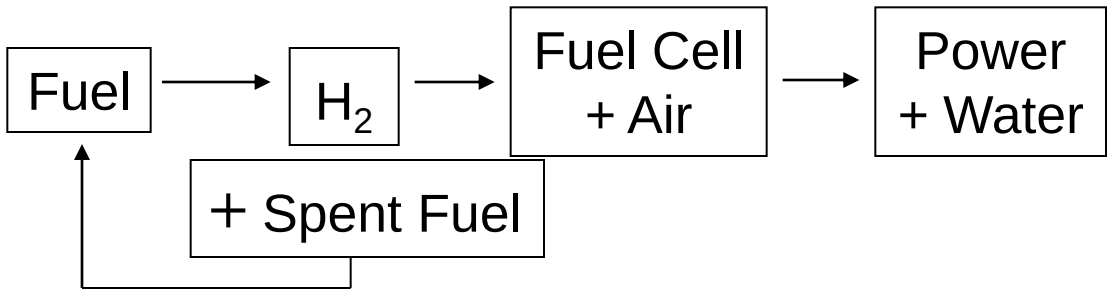
Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876.

Goals of Hydrogen use in Vehicles are Low Emissions and Renewable Fuel

- Low volumetric storage capacity of liquid hydrogen can be supplemented by reversible sorbents or metal hydrides

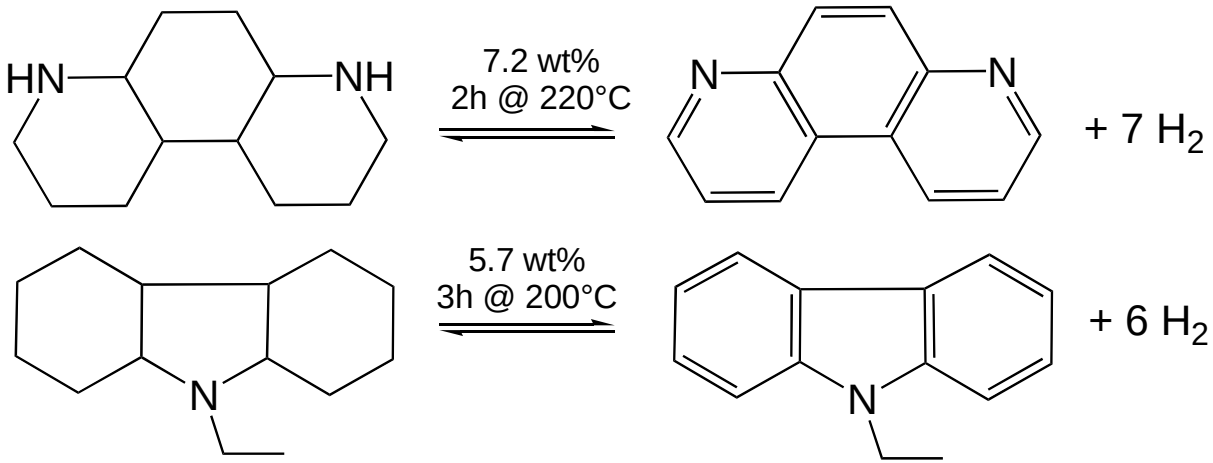


- High storage capacity advantage of chemical hydrides is offset by need to efficiently regenerate spent fuel



Liquid Hydrogen Carriers

- Offers use of current service station fueling infrastructure and avoids need to transport hydrogen.
- Methanol and ammonia have high storage capacities but high dehydrogenation enthalpies and activation energies.
- Air Products (also Crabtree, Jessop and Jensen) are investigating azacycloalkanes with $\Delta G \approx O$ but rates are still too slow and temperatures too high.

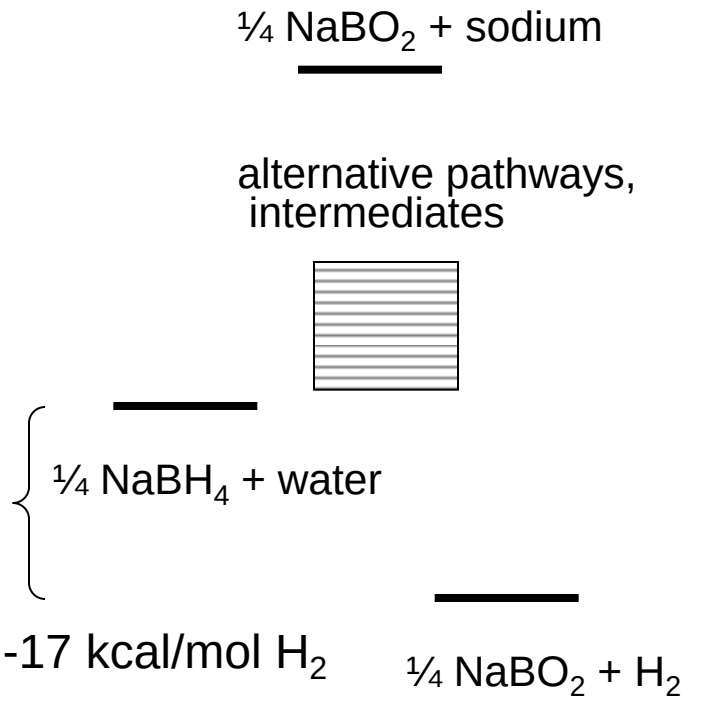


Hydrogen from B-H Bond Hydrolysis

- Heterogeneous Ru-catalyzed hydrolysis has been commercialized as Hydrogen on Demand® by Millennium Cell; used in the Natrium™ car

$$NaBH_4 + 4\,H_2O \rightarrow Na[B(OH)_4] + 4\,H_2 \quad (7.6\ wt\%\ H_2)$$

- Chandra and Xu improved fuel shelf life and reduced cost using ammonia-borane hydrolysis with solid acid catalysts
- Hydrolysis limits hydrogen storage capacity (< 7 wt %) and requires energy-intensive transformation of borate to borohydride



Currently use 1940's Schlesinger technology for B-O to B-H

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DOE's Chemical Hydrogen Storage Center

A coordinated approach to identify, research, develop and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet 2015 goals

- Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways
- Assess concepts and systems using engineering analysis and studies
- Develop life cycle inventory and demonstrate a 1 kg storage system

- More efficient B-OH to B-H regeneration
- Alternative boron chemistry to avoid thermodynamic sinks using polyhedral boranes (BxHy) or amine-boranes
- Concepts using coupled endo/exothermic reactions, nanomaterials, heteroatom substitution for thermodynamic control

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ROHM AND HAAS

MILLENNIUM CELL

BORAX

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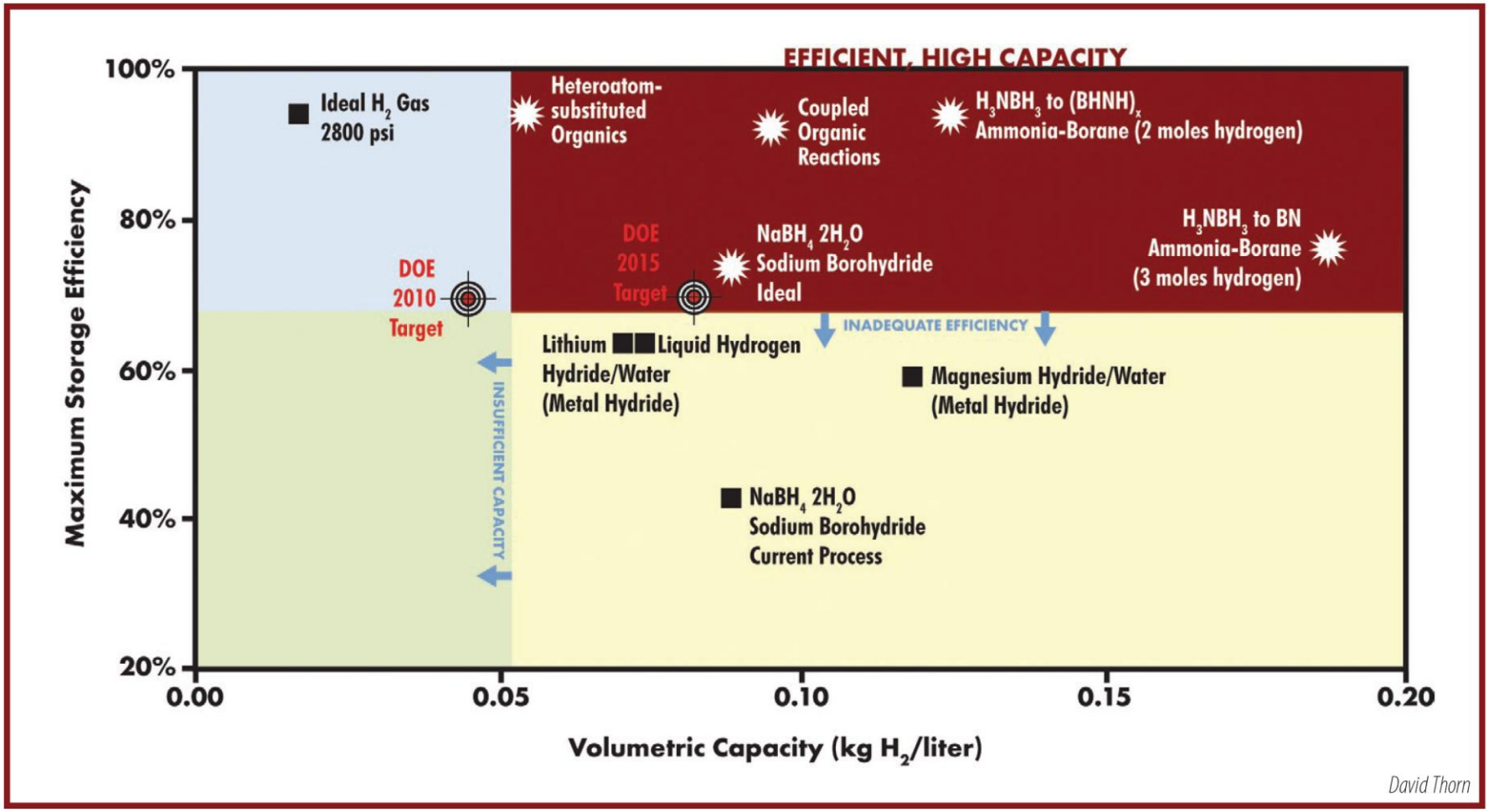
Which Chemical Hydride?



$$H_3NBH_3 \rightarrow n\,H_2 + (H_2NBH_2)_n \rightarrow n\,H_2 + (HNBH)_n \rightarrow n\,H_2 + BN$$

Ammonia-borane	6.5 wt%	13.1 wt%	19.6 wt%

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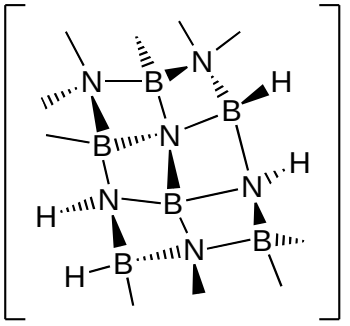
Hydrogen Production Using Ammonia-Borane: Selectivity

$[-H_2N\text{-}BH_2\text{-}]_n$ — acyclic polymer

$\xrightarrow{-H_2}$

$[-HN{=}BH-]_n$ — polymer

$\xrightarrow{-H_2}$



‘diamondoid’

→ cubic BN

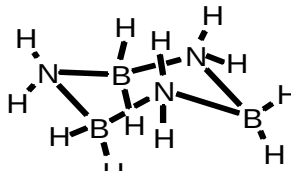
$-H_2$ ↑

$H_3N\text{-}BH_3$ $\xrightarrow{\textbf{-3 H}_2}$ **BN** 19.6 wt % H

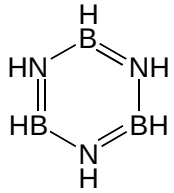
$\Delta H_{AB\text{->}PB}$ = -7.5 kcal/mol H_2

$-H_2$ ↓ $\Delta H_{calc'd}$ = -6 kcal/mol, $\Delta G_{calc'd}$ = -13 kcal/mol

D. Camaioni, PNNL

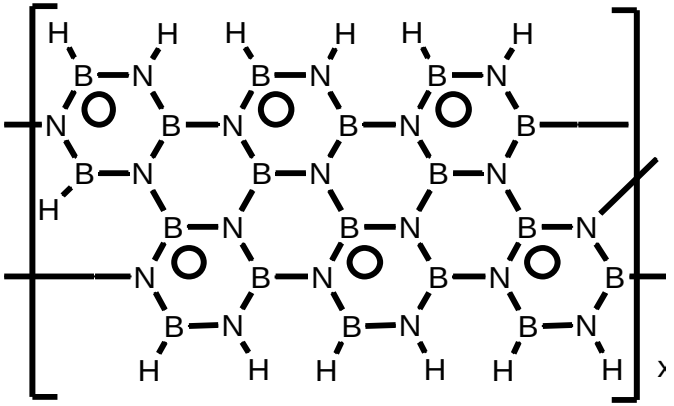


$\xrightarrow{-H_2}$ ΔH = -1, ΔG = -10



$\xrightarrow{-H_2}$ ΔH = -10

G. Ceder, MIT



cyclic trimer ‘cyclotriborazane’

cyclic trimer ‘borazine’

‘graphitic’ polyborazylene (PB)

→ hexagonal BN

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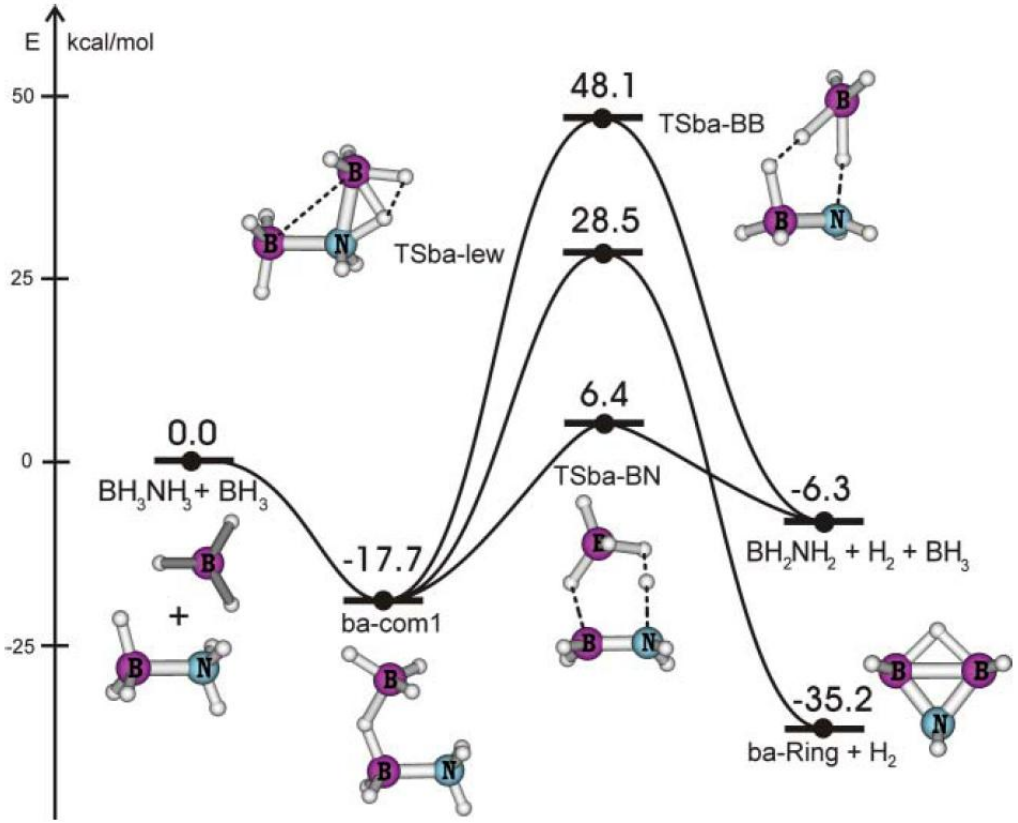
Gas Phase Dehydrogenation of AB

- In a high level CCSD(T) calculation Dixon et al. found that the B-N bond dissociation energy (26 kcal/mol) is less than the barrier for intramolecular hydrogen loss (37 kcal/mol)!



They then showed that catalysis by BH_3 drastically reduces the barrier to hydrogen loss to 6.4 kcal/mol

J. Phys. Chem. A **2007**, *111*, 679.

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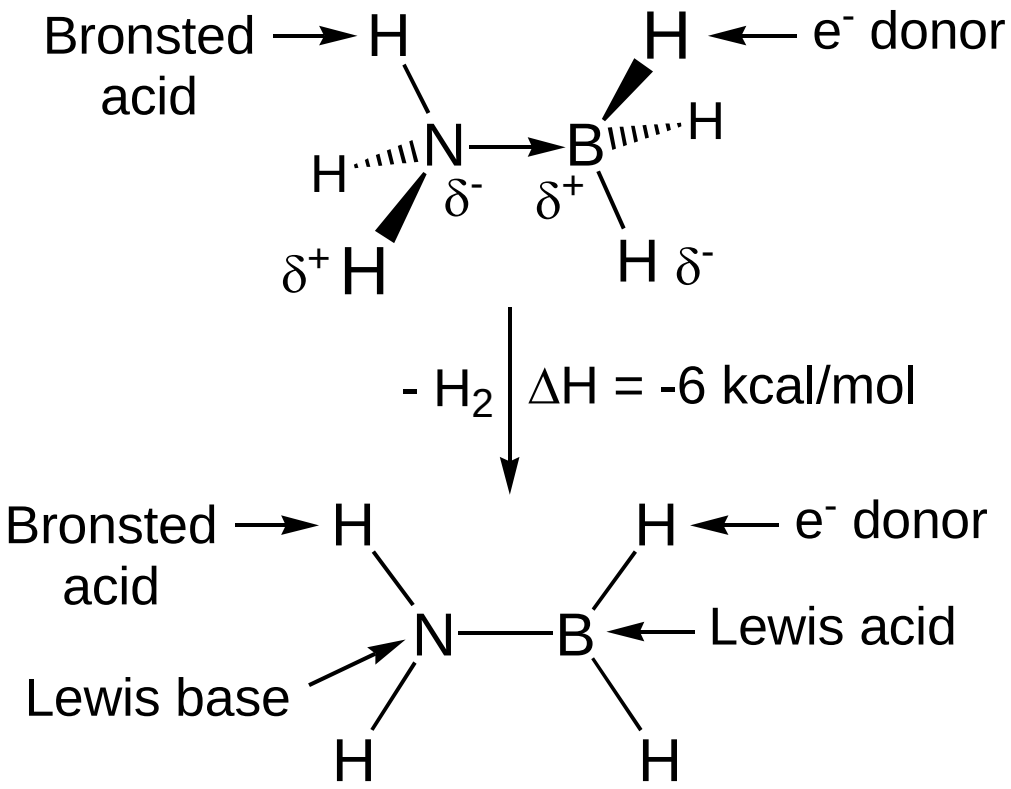
Ammonia Borane vs. Ethane

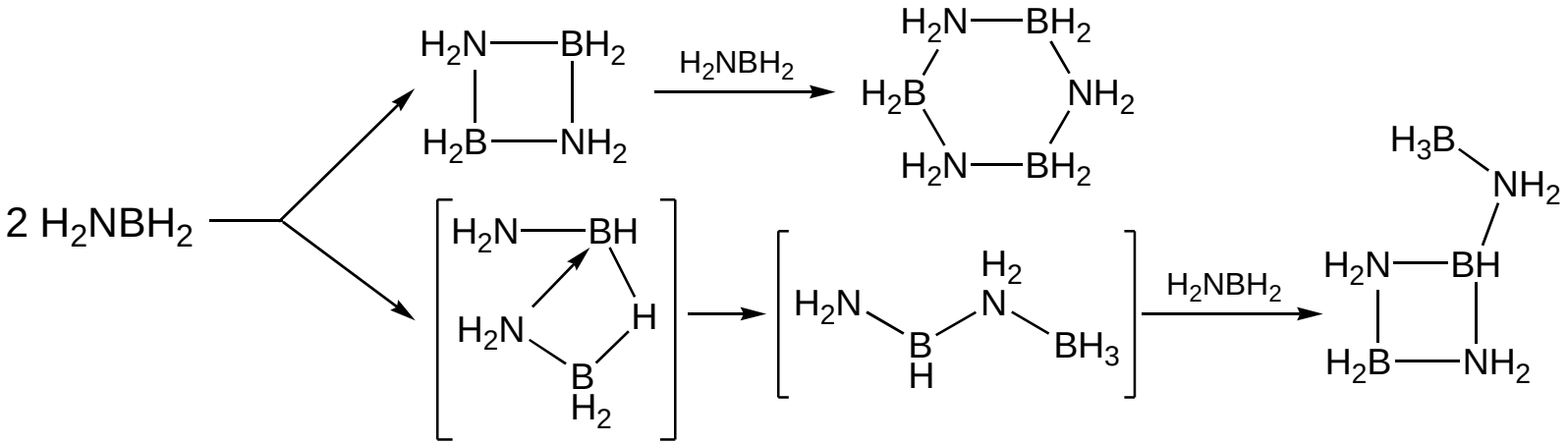
- Unlike ethane, dehydrogenation of ammonia-borane to aminoborane is exothermic
- Polar B-N compounds are multifunctional



Element	Electro-negativity
C	2.5
H	2.1
B	2.0
N	3.0

Aminoborane is Reactive Molecule

- In low T matrix H_2NBH_2 oligomerizes above -150° C
- In solution two oligomerization pathways operate:

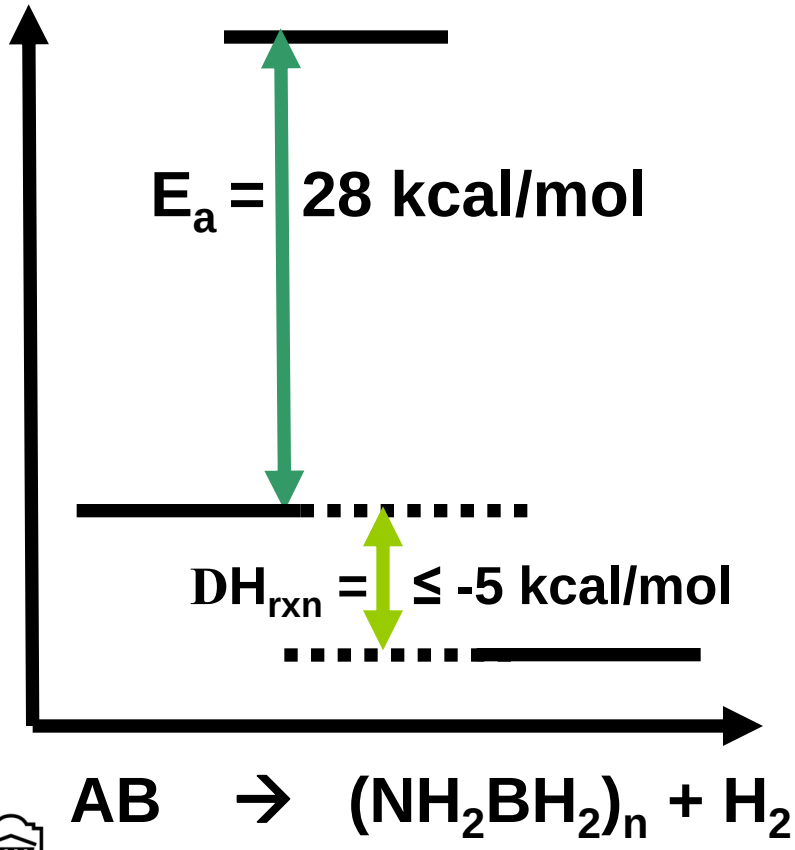


- Thermal dehydrogenation of ammonia-borane in solid state proceeds through cationic $[H_2B(NH_3)_2]^+(BH_4)^-$ initiator to afford insoluble 'graphitic' polyborazylene (BN cross-linked borazine, BNH_x)

Thermolysis of Solid Ammonia-Borane

(1) $H_3NBH_3 \rightarrow (H_2NBH_2)_n + H_2$ 90-100˚C

(2) $(H_2NBH_2)_n \rightarrow (HNBH)_n + H_2$ 120-160˚C



- Use of slow heating rate prevents formation of volatile cyclic products
- Compare ΔH = -5 vs. -6 kcal/mol for formation of cyclic trimer
- Insoluble, presumably cross-linked $(HNBH)_n$ needs detailed solid-state NMR characterization

J. Baumann, G. Wolf, F. Baitalow et al. *Thermochim. Acta* **2000**, **2002**, **2005**.

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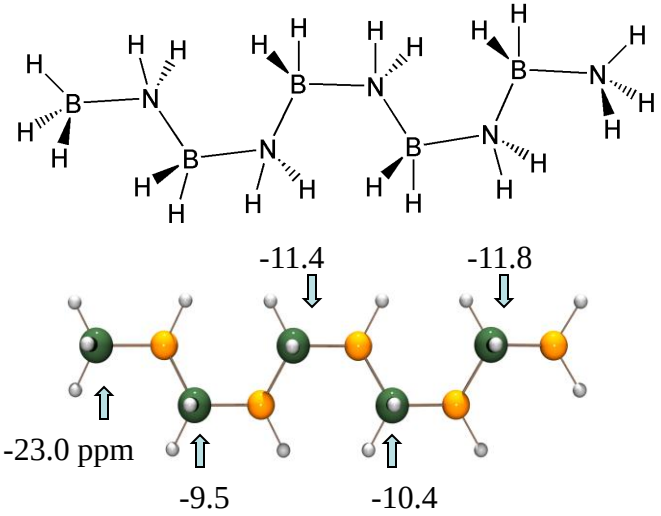
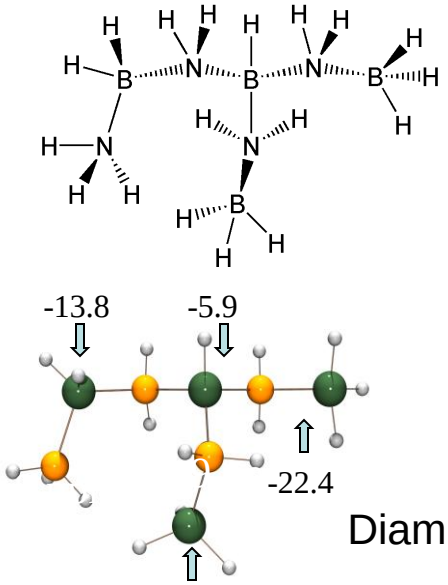
DFT/GIAO/B-11 NMR Polymer Characterization

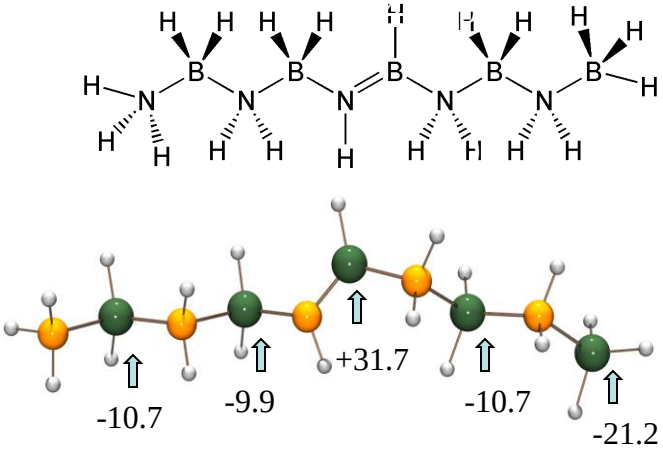
Polyaminoborane



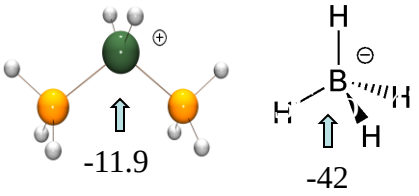
Branched chain polyaminoborane

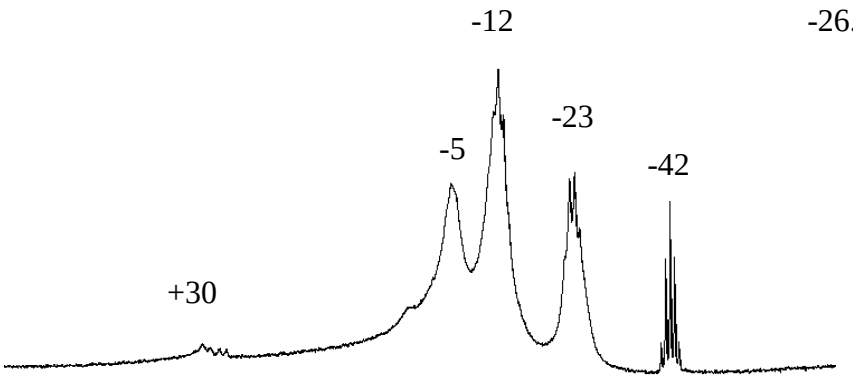


Unsaturated polyaminoborane



Diammoniate of diborane: $[H_2B(NH_3)_2]BH_4$





B-11 NMR spectrum of $[H_2BNH_2]_n$ in pyridine

- NMR results suggest formation of both dadb and branched oligomer

Sneddon group, Penn Chemistry

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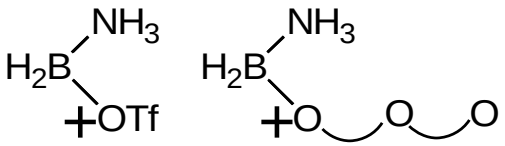
Acid-Initiated Ammonia Borane Dehydrogenation

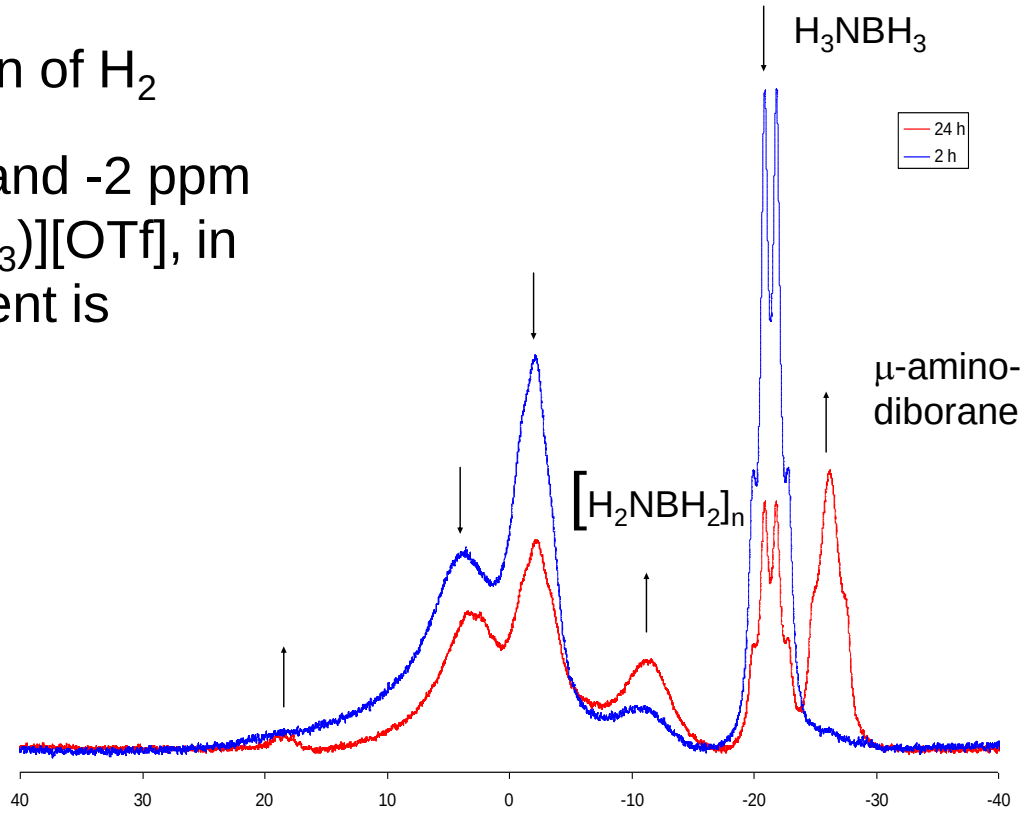
- Strong Lewis or Brønsted acids release H_2 at 25° C

- Addition of HOTf results in immediate, copious evolution of H_2

- ^{11}B NMR resonances at 4 and -2 ppm are consistent with $[H_2B(NH_3)][OTf]$, in which the OTf anion or solvent is coordinated to the boron



- Similar reactions using $B(C_6F_5)_3$ give similar cation as $[HB(C_6F_5)_3]^-$ salt due to H^- abstraction from H_3NBH_3



H_3NBH_3 + 10 mol% triflic acid in diglyme

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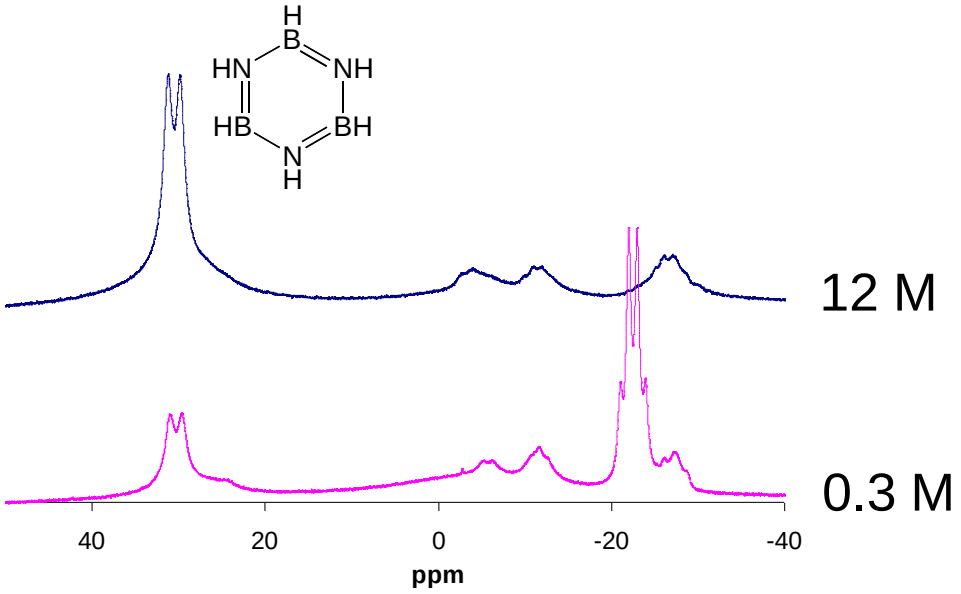
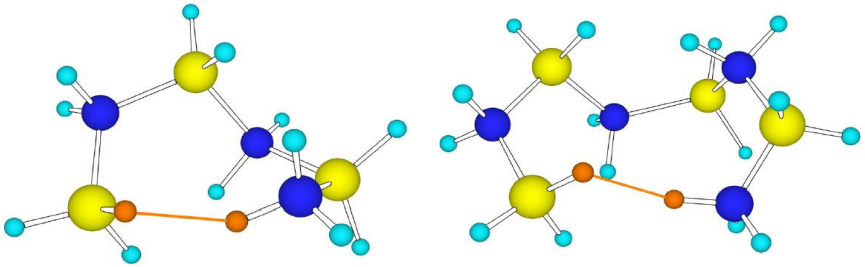
Rates More Practical with Less Solvent

- Why are aminoborane oligomers less thermally stable in solution than solid state?
- Calculations suggest instability arises from large dipole moments
- Simulation of annealing with QM forces reveals coiled structure of oligomers, with small dipole moments, stabilized by dihydrogen bonds – precursors to cyclic products



H_3NBH_3 + 0.5 mol% $B(C_6F_5)_3$ heated at 80° C for 4 h in diglyme



$H_3B[H_2NBH_2]_{2,3}NH_3$ *J. Li and M. Gutowski, PNNL*

- Ionic liquid solvents stabilize acyclics, affording cross-linked BNH_x *L. Sneddon et al. JACS*, **2006**.

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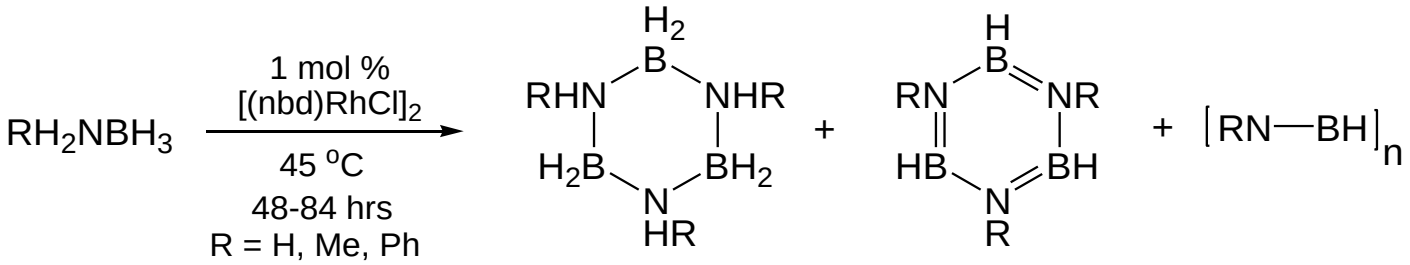
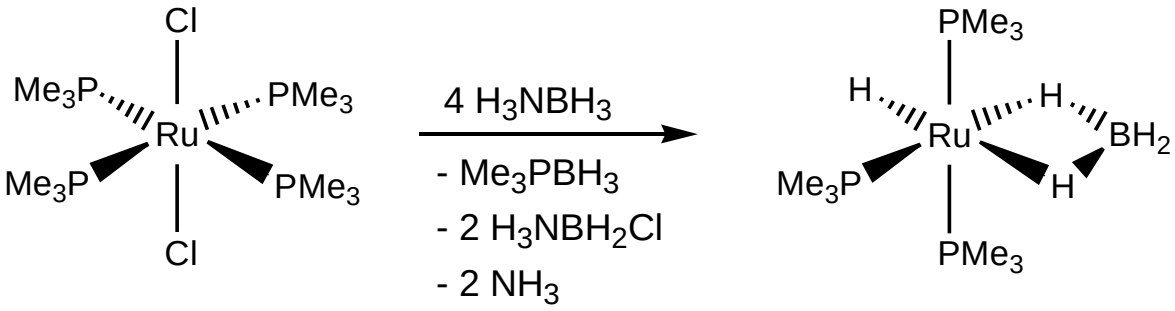
Metal-Catalyzed Ammonia-Borane Dehydrogenation

- Rh catalyst gives mixture of cyclics (major) and 'polymer' (minor). Catalyst solution turns black and heterogeneous during reaction with slow AB dehydrogenation (days)

I. Manners *et al.*, *J. Am. Chem. Soc.* **2003**, *125*, 9424.



- Electron-rich Ru-PMe_3 catalyst is stable under reaction conditions but reaction is slow and selectivity poor R. T. Baker *et al.*, unpublished results.



Metal Complex-Catalyzed Ammonia-Borane Dehydrogenation

- Effective ammonia-borane (AB) dehydrogenation catalysts fall into two classes:

  Class 1: Fast release of one equiv. of H_2 per AB and formation of insoluble aminoborane pentamer, $(NH_2BH_2)_5$

  e.g. $IrH_2[2,6\text{-}(OPBu^t)_2C_6H_3]$ (Goldberg, Heinekey *et al.*, *JACS*, **2006**)

  $RuCl_2(Bu^t{}_2PCH_2CH_2NH_2)_2/KOBu^t$ (Fagnou *et al.*, *JACS*, **2008**)

  $RuH(PMe_3)[N(CH_2CH_2PPr^i{}_2)_2]$ (Schneider *et al., Angew. Chem.*, **2009**)

  $Fe(dpen\text{-}H_2)(dcpe)$ (Baker *et al.*, unpublished)

  Class 2: Slower release of > 2 equiv. of H_2 and formation of B-N cross-linked borazine [polyborazylene, (BNH_x)]

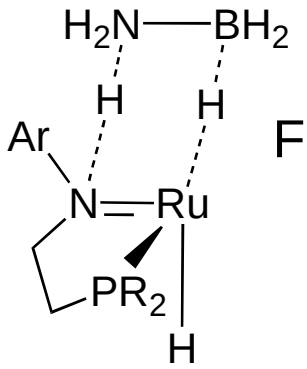
  e.g. $[RhCl(1,5\text{-cyclooctadiene})]_2$ (Manners *et al. JACS*, **2003**)

  Ni(*N*-heterocyclic carbene) (Baker *et al., JACS*, **2007**)

What factors determine the rate and extent of hydrogen release?

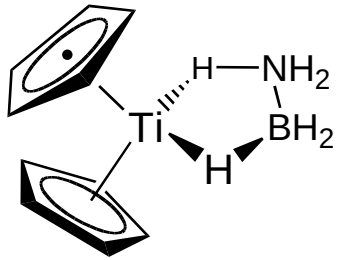
Bifunctional Activation of B-H / N-H Bonds

- Current computational chemistry studies invoke initial coordination via M-H-B, followed by protonation of filled metal orbital, metal hydride or ligand ‘lone pair’



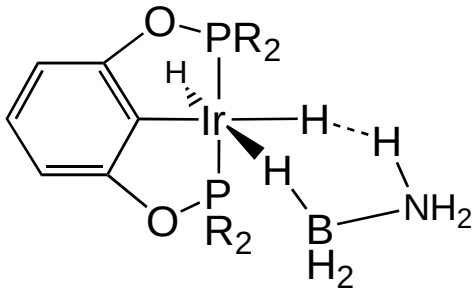
Fagnou, Gorelsky *et al.*

J. Am. Chem. Soc. **2008**



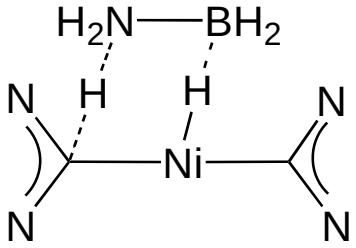
Luo and Ohno

Organometallics **2007**



Paul, Musgrave *et al.*

Angew. Chem. Intl. Ed. **2007**

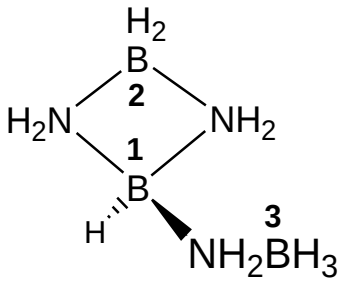


Yang and Hall

J. Am. Chem. Soc. **2008**

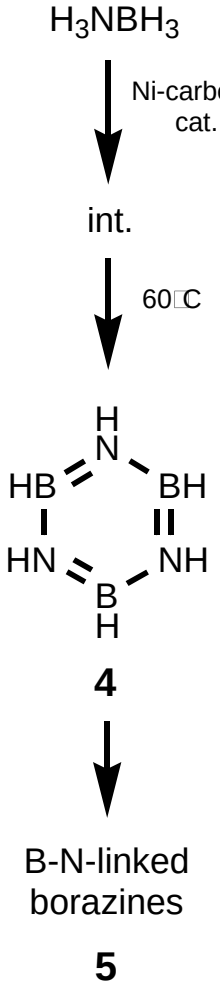
Beyond Aminoborane: Identification of a Stable Intermediate

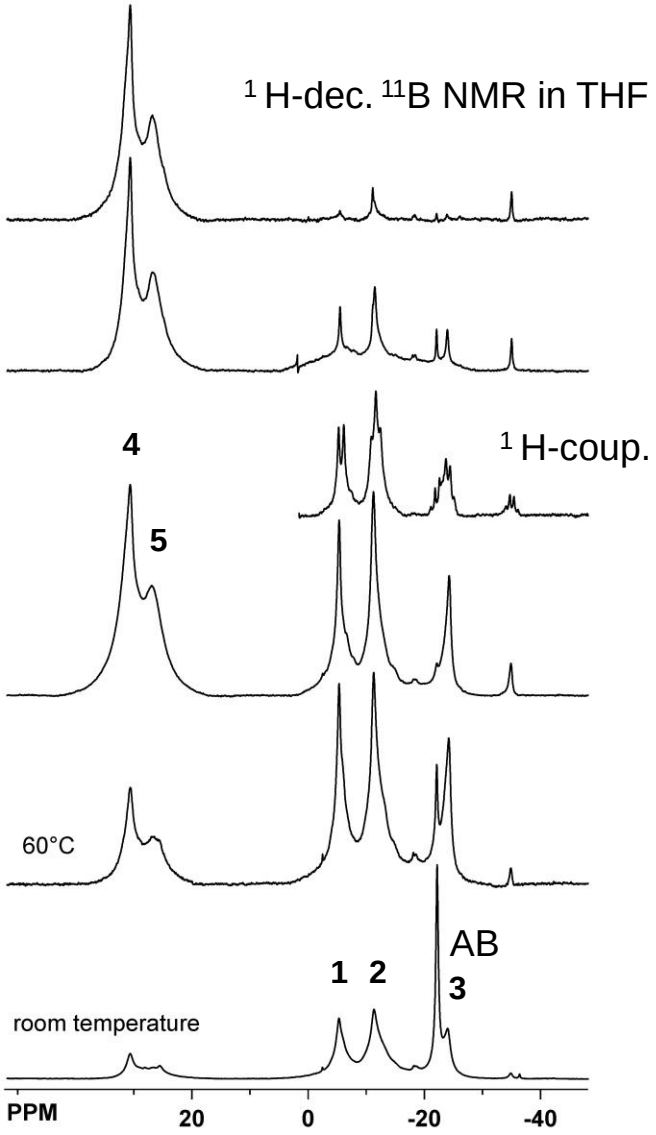
intermediate



calc. chem. shifts (DFT):
B1: -4.4
B2: -11.2
B3: -23.8 ppm

How is this stable intermediate formed?





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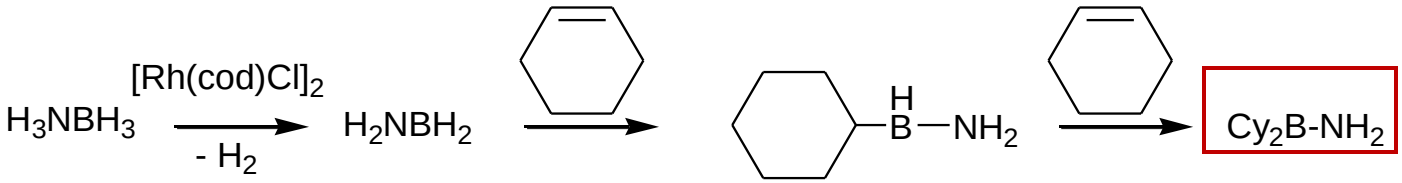
Aminoborane Trapping Experiments



^{11}B NMR: 47.5 ppm

- Rh-catalyzed AB dehydrogenation in cyclohexene/THF affords high yields of aminodicyclohexylborane instead of aminoborane- and iminoborane cyclic oligomers

- Under the same reaction conditions, Ir and Cr catalysts afford only aminoborane cyclic oligomers!

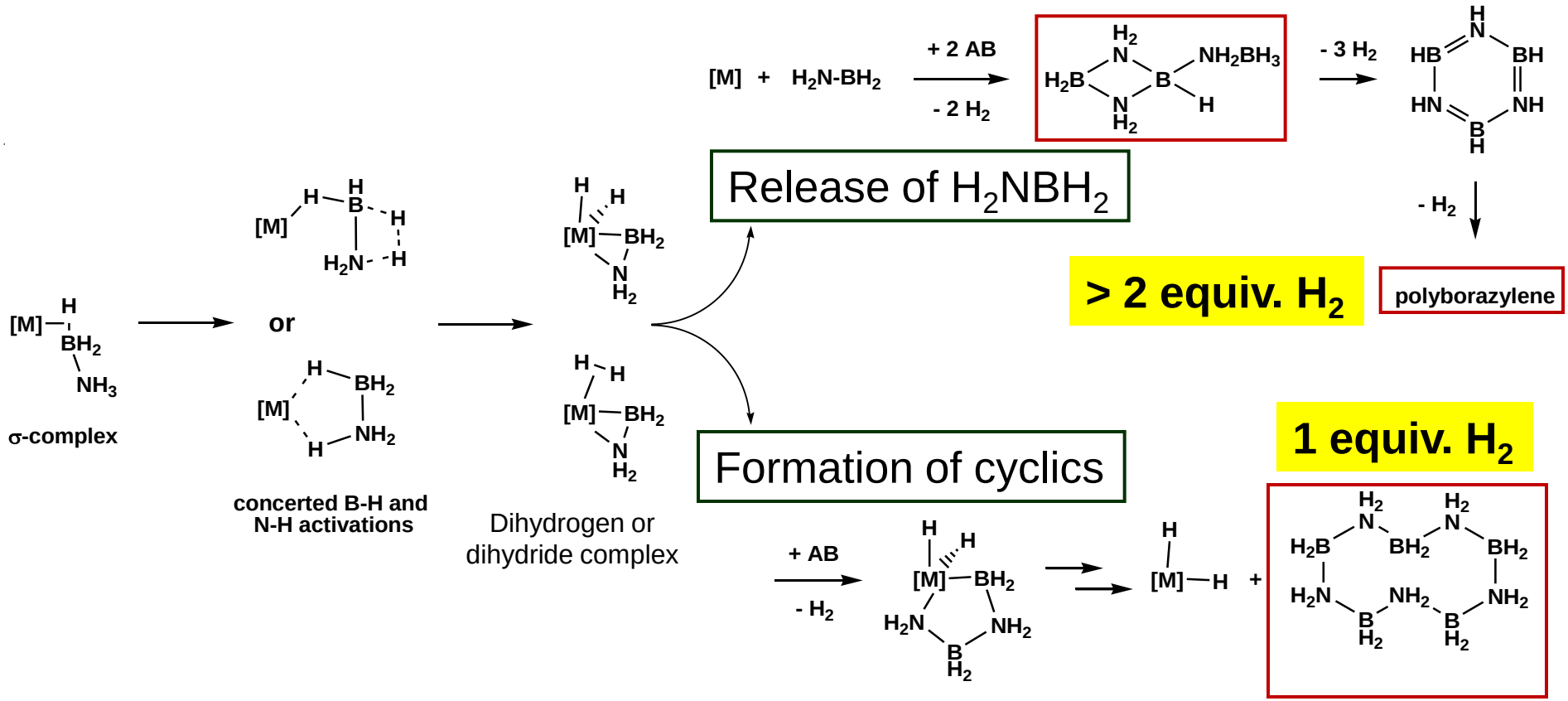
Will heating liberate metal-coordinated aminoborane?

Temperature Effect on the Release of BH_2-NH_2: Cyclics vs. Polyborazylene

T	[cat]	Main BN products formed (diglyme or THF)	Equiv. H_2	Trapping of NH_2BH_2 (cyclohexene)
298 K	$(CO)_5Cr(NMe_3)$	$(NH_2BH_2)_3$	1	No
298 K	$(POCOP)Ir(H)_2$	$(NH_2BH_2)_5$	1	No
298 K	$[Rh(cod)Cl]_2$	polyborazylene	>2	Yes
333 K	$(CO)_5Cr(NMe_3)$	polyborazylene	>1	Yes
333 K	$(POCOP)Ir(H)_2$	$(NH_2BH_2)_5$ + polyborazylene	>1	Yes
333 K	$[Rh(cod)Cl]_2$	polyborazylene	>2	Yes

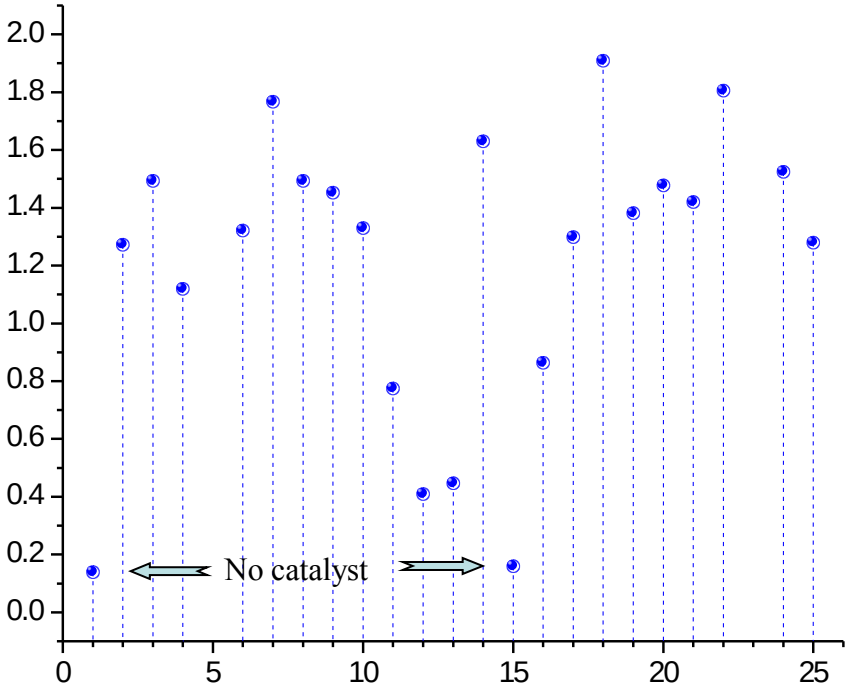
$(BH_2NH_2)_n$ cyclics are formed within metal coordination sphere!

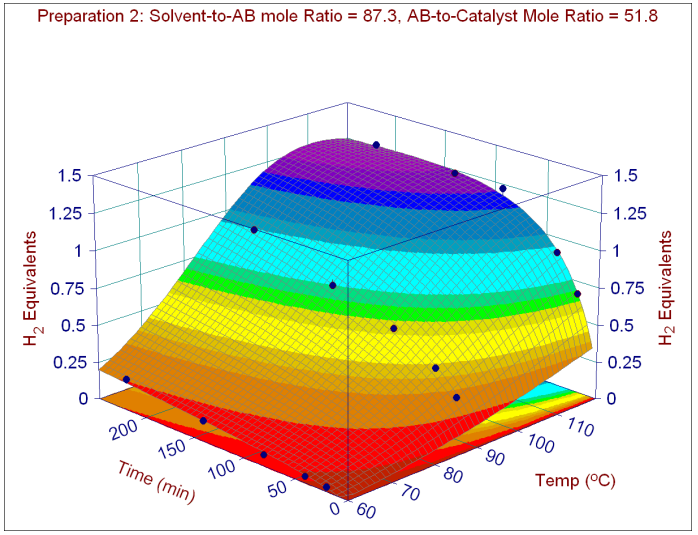
AB Dehydrogenation Selectivity Dictates Extent of H_2 Release



- Release of H_2NBH_2 and formation of BN-ethylcyclobutane intermediate are key to greater hydrogen release
- Formation of borazine and cyclics not yet fully understood

Hydrogen Quantification at Los Alamos





✓ 25 samples per run allows for rapid evaluation of catalysts, kinetics and reaction conditions

• In above run most catalysts afforded 1.3 - 1.5 equiv. H_2 / AB due to simultaneous operation of both reaction pathways

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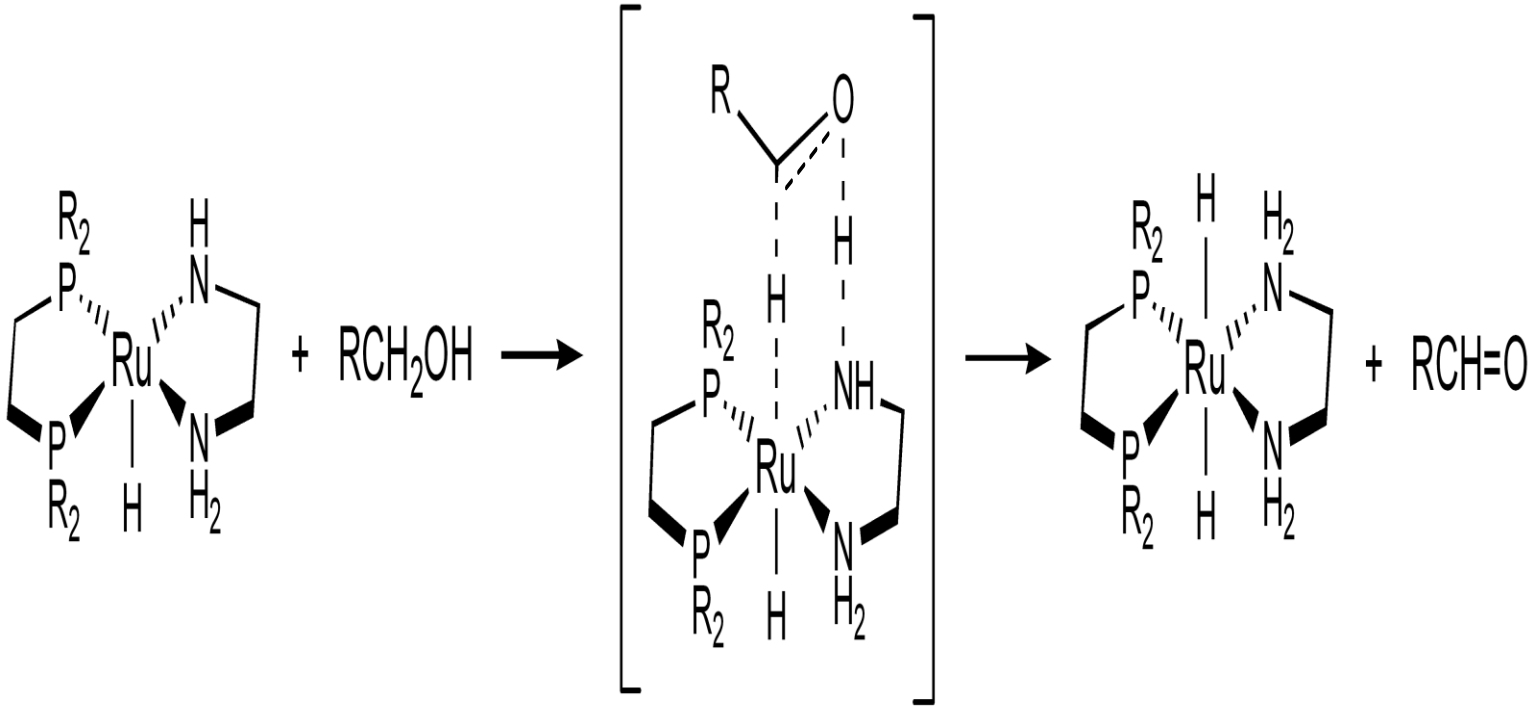
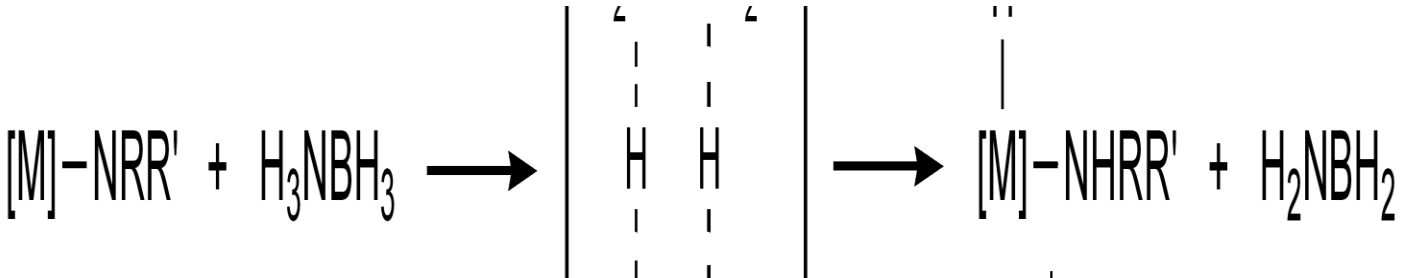
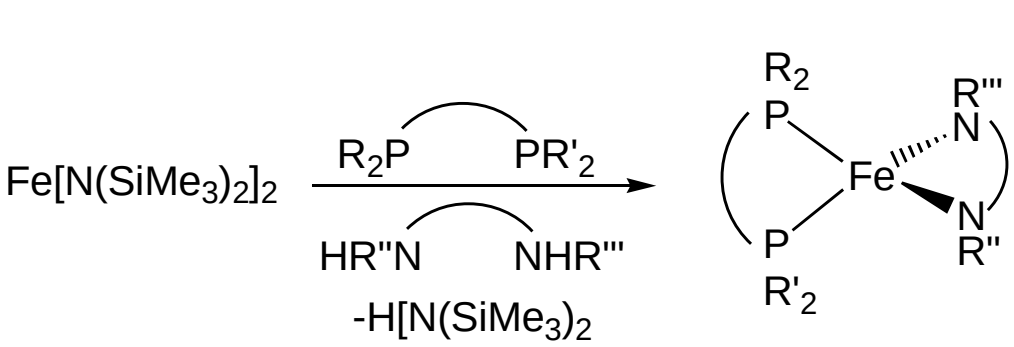
Ligand-Assisted Dehydrogenation

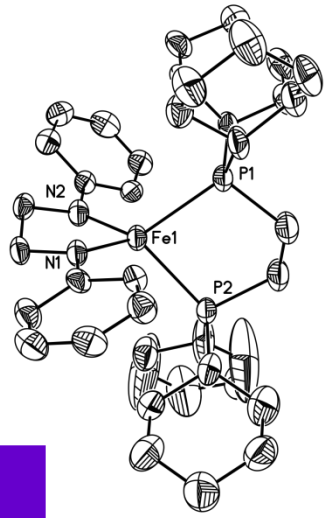
- Noyori and others showed that metal amido catalysts dehydrogenate alcohols via ligand-assisted heterolytic cleavage





Modular Iron Amido Dehydrogenation Catalysts

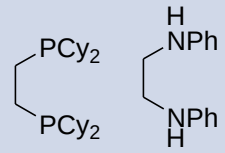


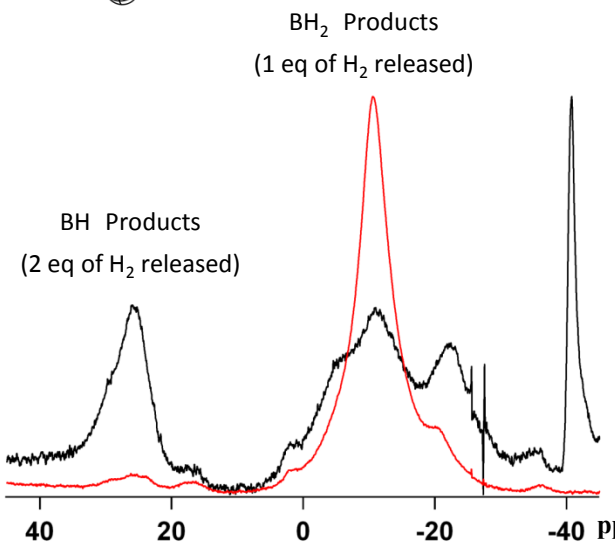


$^{11}B\{^{1}H\}$ MASNMR Spectra

$Fe[N(SiMe_3)_2]_2(PCy_3)$

Fe(dcpe)(dpen-H_2)

Ligand(s)	Catalytic activity for AB dehydrogenation
 dcpe dpen	Complete consumption of AB after 15 min (5% cat. loading, THF, RT) or 2 h (1.2% cat. loading, THF, RT). Forms $(-BH_2NH_2-)_5$ product, 1 eq. of H_2 per AB Similar results obtained by Fagnou *et al.* (*JACS,* **2008** and Schneider *et al. (Angew. Chem.*, **2009**).
PCy_3 (3 eq.)	Formation of borazine, polyborazylene and $(-BH_2NH_2-)_5$ in 3:1:5 ratio (2% cat. loading, THF, 60 ºC)



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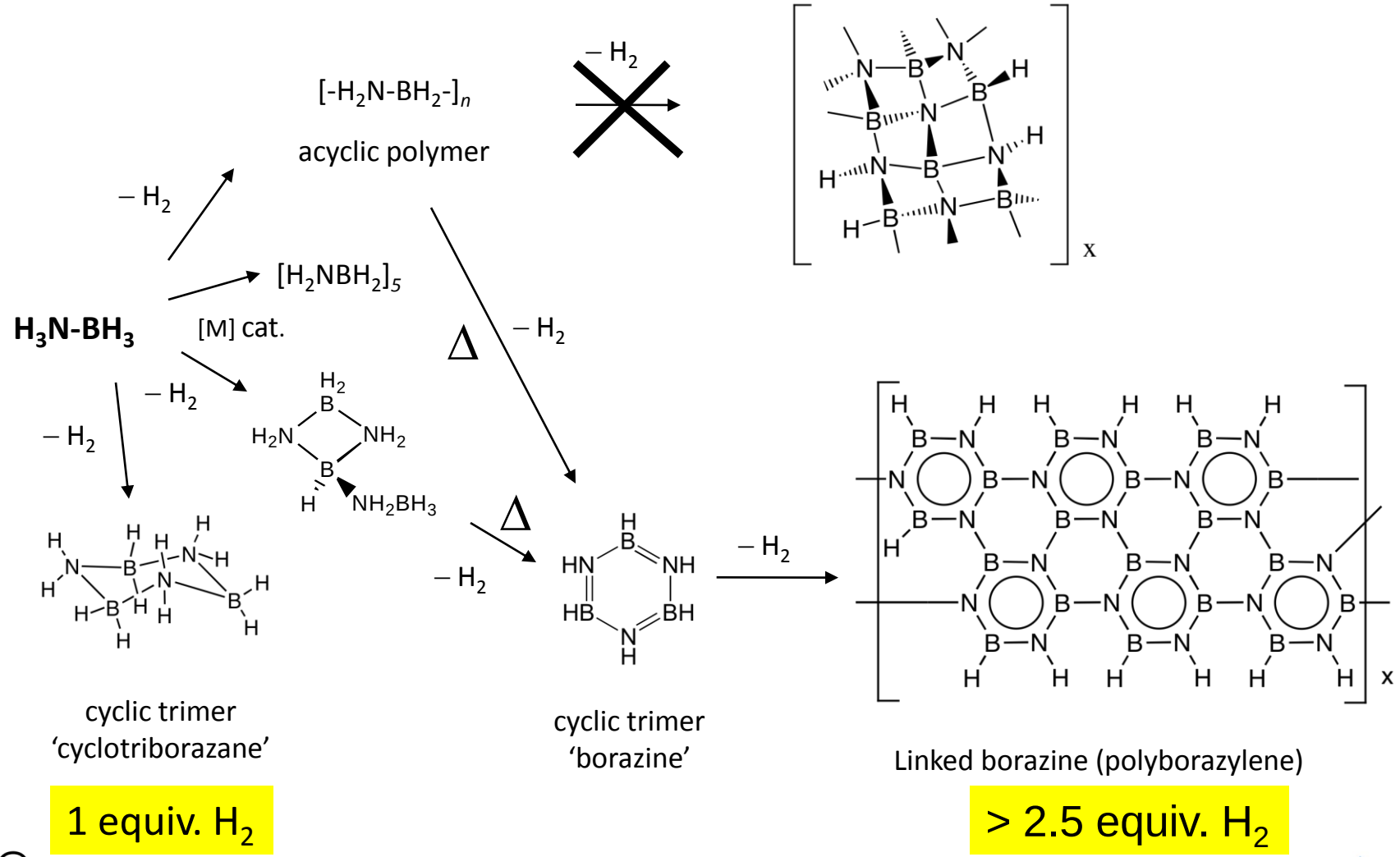
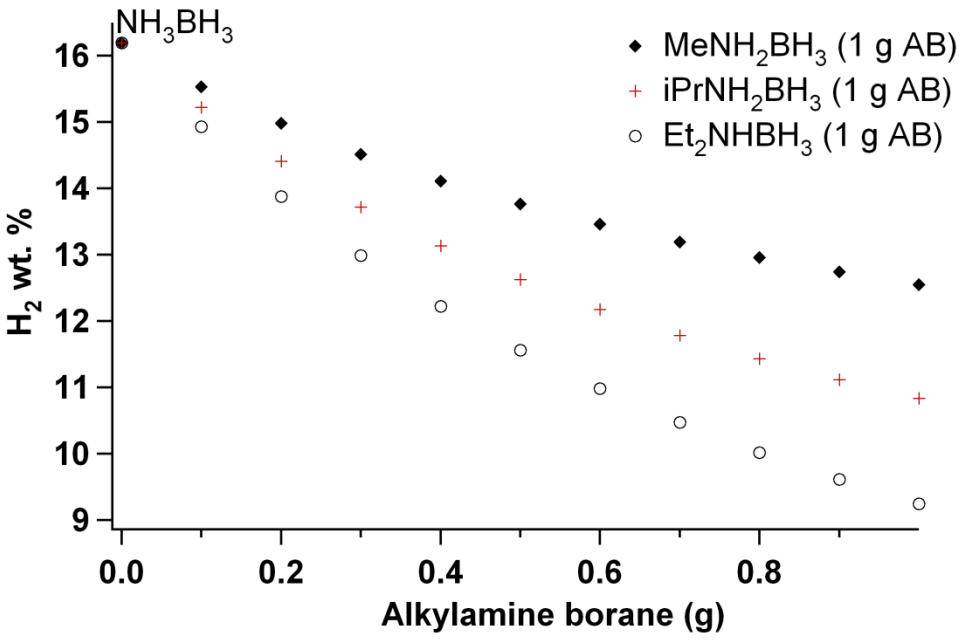
Hydrogen Production Using Ammonia-Borane: Selectivity

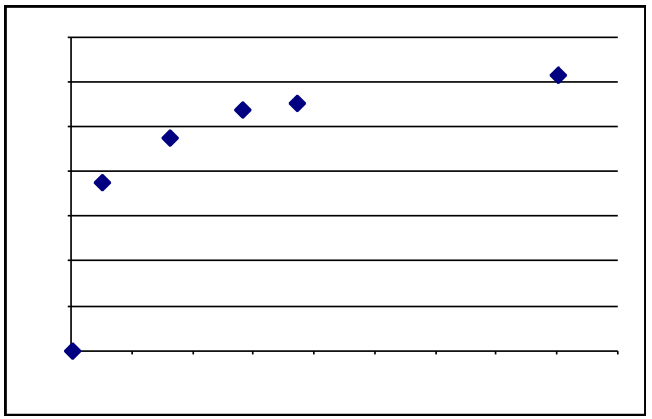


Liquid Amine-Borane Fuels

- Liquid mixed amine-borane fuels mitigate capacity loss due to non-hydrogen releasing solvents (Nippon Oil patent 2004)

$$H_2RNBH_3 \Longrightarrow [HRNBH_2]_3 + 2\,H_2$$





✓ Preliminary experiments with 5 mol% Ni carbene cat. in 1:1 AB:MeAB at 60° C gave 5.7 wt% hydrogen vs. 10.5 wt% theoretical

Need to optimize catalysts in amine-borane solvents

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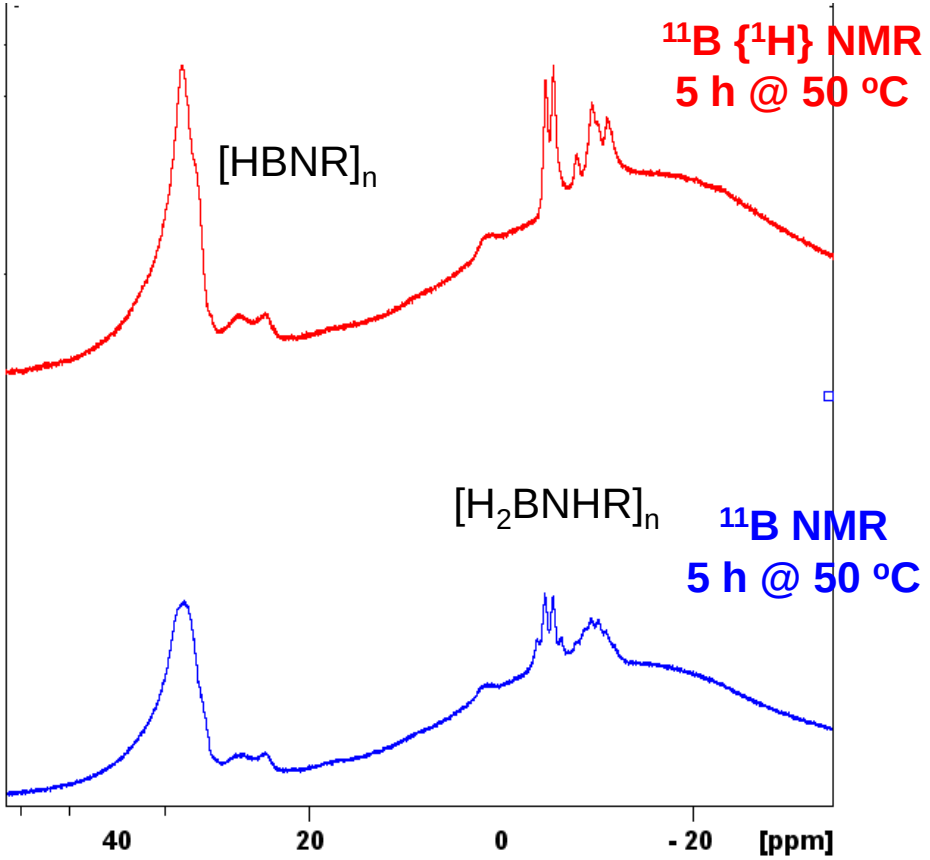
Catalyzed Hydrogen Release from a Liquid Amine-Borane Fuel Blend

- Catalyzed dehydrogenation of amine-borane mixture (ca. 8 wt% H) remains liquid throughout reaction

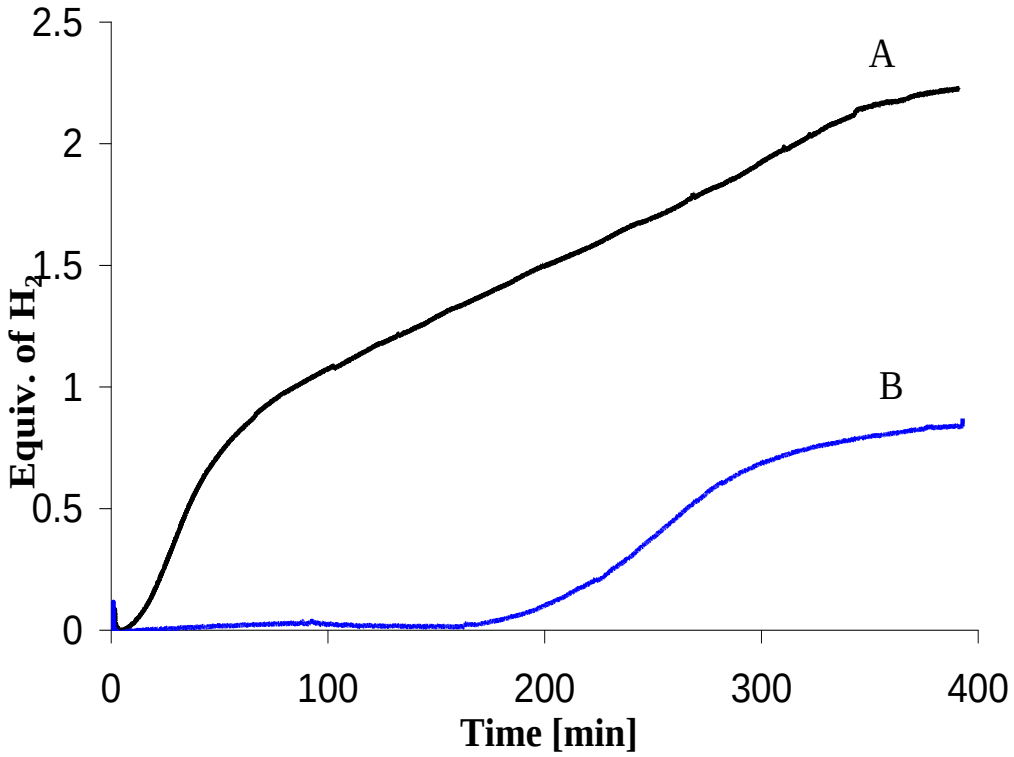
- Current work involves:
  - determining highest practical working concentration of ammonia-borane;
  - identifying optimal base-metal heterogeneous catalyst;
  - assessing purity of H_2 stream

25 wt% H_3NBH_3 in RH_2NBH_3 + 2 mol% RhCl(diene) catalyst



Dehydrogenation of NH_3BH_3 in Ionic Liquids (ILs)

Contrasting dehydrogenation at 85 ^{0}C



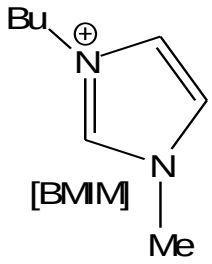
(A) 50 wt% solution of NH_3BH_3/[BMIM][Cl]

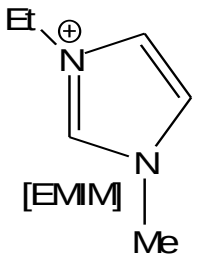
(B) Solid NH_3BH_3

L. G. Sneddon, *et al., J. Am. Chem. Soc.*, **2006**, *128*, 7748.

Ionic Liquids Change Catalyst Activity and Selectivity

Ammonia-borane dehydrogenation with $RuCl_2(PMe_3)_4$ (Tf = O_2SCF_3)





NH_3BH_3

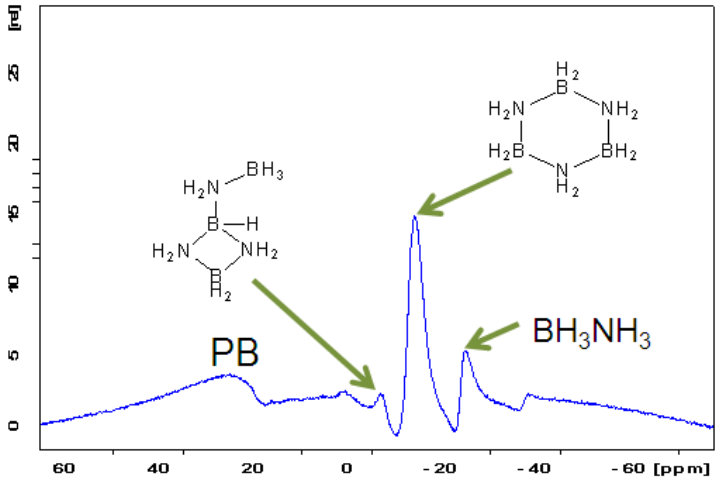
0.6% Ru, 298K, 48 h

[EMIM][O_3SOEt]

[BMIM][NTf_2]

[BMIM][OTf]

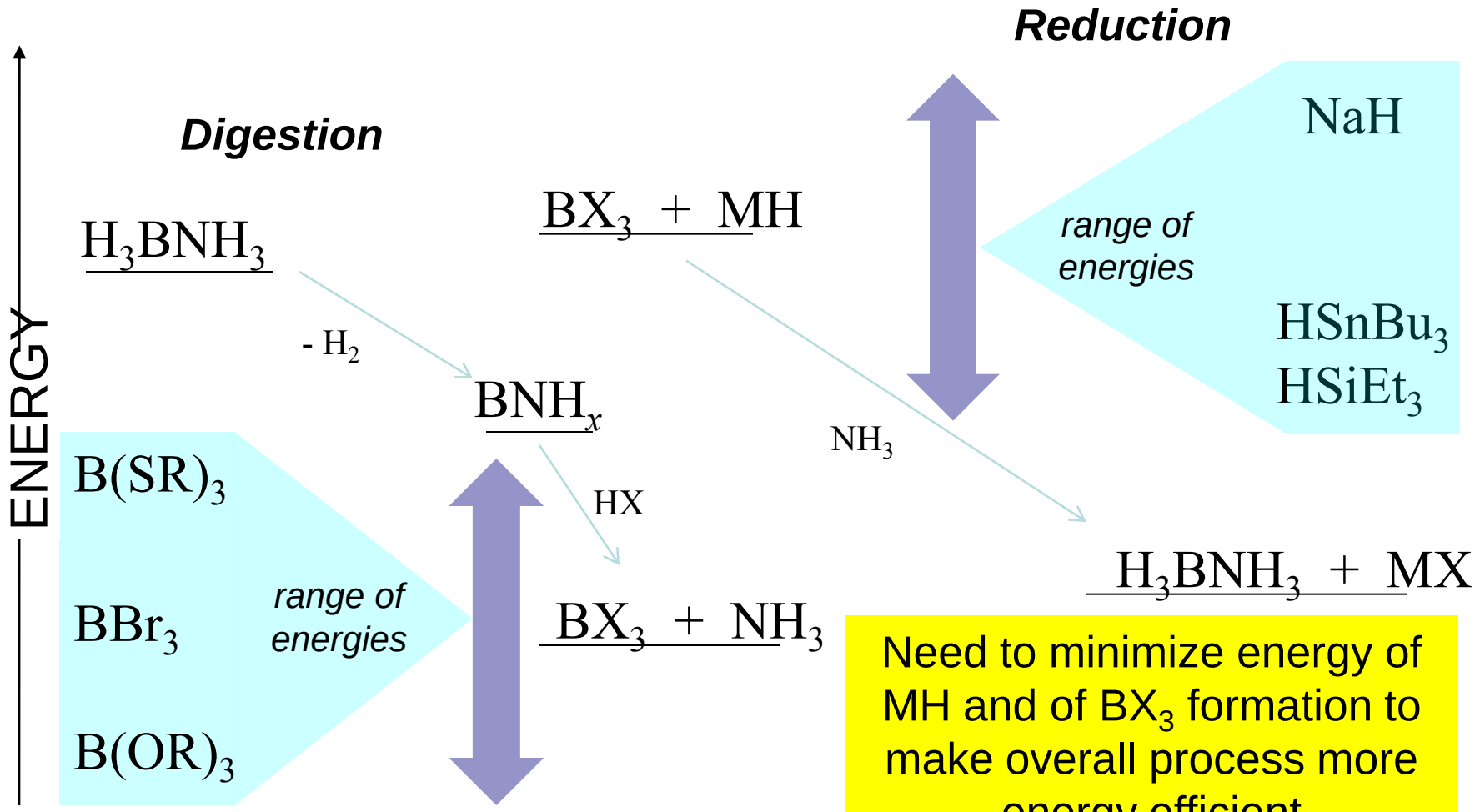
Trace $B_3N_3H_6$ Trace H_3BPMe_3 White Solid	$B_3N_3H_{12}$ White Solid	Polyborazylene, ECB analog, $B_3N_3H_{12}$ **No White Solid**



^{11}B NMR of Ru-catalyzed AB dehydrogenation in [EMIM][O_3SOEt]

- Why does ethylsulfate anion increase selectivity?

Ammonia-Borane Regeneration: Matching Digestion/Reduction Energetics

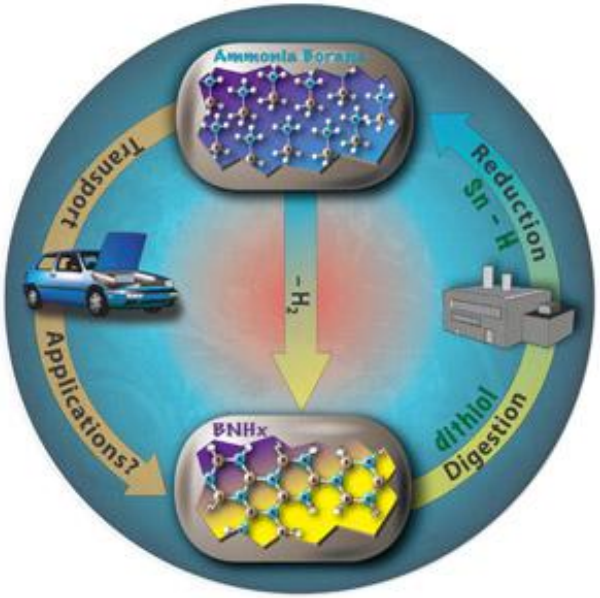


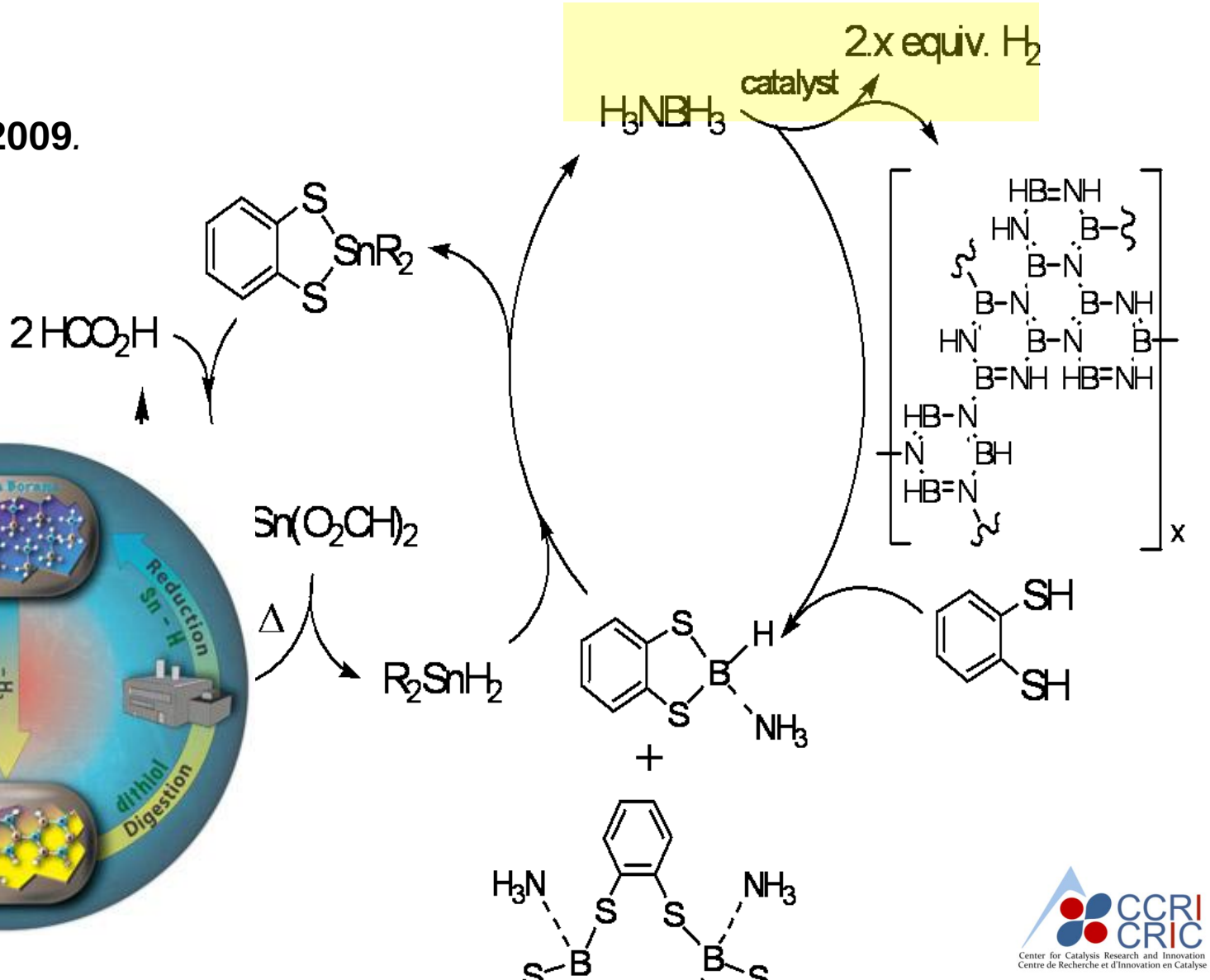
Need to minimize energy of MH and of BX_3 formation to make overall process more energy efficient

Experiment guided by theory (Alabama)

Progress Toward Energy-Efficient AB Regeneration

B. L. Davis et al.
Angew. Chem. **2009**.





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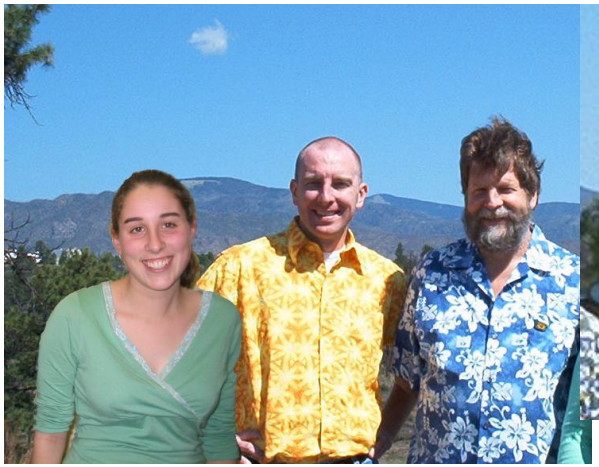
Conclusions

- Ammonia-borane is a promising hydrogen storage material
  - significant progress being made on high rate and extent of hydrogen release and energy-efficient regeneration of polyborazylene 'spent fuel'
- Wide range of mechanisms proposed for initial AB dehydrogenation step
  – need additional detailed kinetic studies to provide additional catalyst design criteria for faster rates
- Extent of hydrogen release depends on efficient ejection of reactive aminoborane (NH_2BH_2) from metal coord. sphere
  – need to investigate reactivity of H_2NBH_2 complexes and BN-ethylcyclobutane intermediate using experiment and theory
- Efficient catalysis of borazine cross-linking will limit contamination of hydrogen stream
- Amine-borane fuel blend may afford liquid fuel and spent fuel

Acknowledgements



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Charles Hamilton (QDVision)

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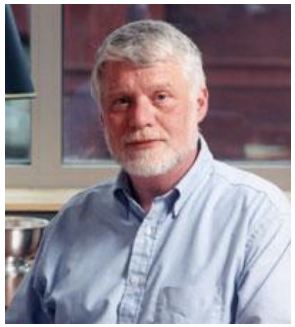
Vincent Pons (Toulouse Law)

Bob Butterick, III and **Larry Sneddon,** Penn Chemistry



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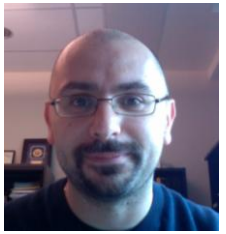

Gianpiero Rachiero

Charlie Kivi

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